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Foliar application of phosphorus compounds

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Foliar application of phosphorus compounds

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TABLE OF CONTENTS

Page

I. INTRODUCTION

Of all the major nutrients, phosphorus is the element in shortest supply in the world economy. It is the one for which agronomists of different countries express the greatest fear of ultimate exhaustion. Unlike many other plant nutrients, phosphorus added to soil as fertilizer generally does not move appreciably from the area of placement. The rapid and tenacious fixation of fertilizer phosphorus added to most soils is general knowledge. Plants recover only a small proportion of the phosphorus supplied as fertilizer. A more efficient method of application would certainly be welcome.

Wittwer (1964) pointed out that present-day terrestrial plants, during their evolutionary development from their origin in the oceans, never lost their ability to absorb nutrients and water through their aerial parts. Interest in foliar nutrition has increased tremendously in the past two decades for several reasons. First, concentrated, highly soluble fertilizers have been developed. Second, superior machines have been developed and are widely used for spraying insecticides, herbicides, and growth regulators. Third, advances have been made in the knowledge of surfactants and other adjuvants and in the knowledge of plant physiology in general. With regard to phosphorus fertilizer, there is an increasing awareness of the low recovery by plants of phosphorus applied to the soil as fertilizer. Moreover, the availability of radioactive phosphorus has facilitated quantitative studies on foliar absorption and translocation.

Foliar fertilization is now an established practice with many crops. Foliar application of nitrogen is very popular with horticultural and fruit crops, where urea is frequently mixed in the sprays. As compared with applications of plant nutrients to soil, foliar fertilization is credited with rapid correction of nutrient deficiencies, more efficient use of fertilizers, and greater control over fruiting and vegetative responses. Plant nutrients may be applied to leaves by use of a high-clearance sprayer or an airplane under circumstances in which incorporation of the nutrients in the soil would not be practicable.

The effective quantity of phosphorus that can be applied to leaves is limited in several ways. First, the solubility of certain sources of phosphorus is low. Second, the volume of solution that will adhere to the foliage and the concentration of phosphorus in solution that can be applied without damaging the leaves are limited.

Phosphorus, to date, has not been used in sprays as much as nitrogen for several reasons. First, many phosphorus compounds have low solubility. Second, the greatest response from phosphorus applied to the soil is frequently early in the season when the leaf area is small. Perhaps the most important reason is the fact that no phosphorus compound has been found which can be applied to the leaves in high enough quantities to contribute significantly to the total phosphorus needs of a crop without causing damage to the leaves. Urea can be applied in much higher concentration. For example, 80 percent of the total nitrogen applied to Hawaiian pineapple fields is applied as urea sprays.

Phosphorus seemingly offers promise for application to leaves because the quantities of phosphorus needed are only one-tenth to one-fifth of the quantities of nitrogen needed. Besides that, the rate of absorption and the mobility in the plant are only a little less for phosphorus than for nitrogen.

The objectives of the work reported in this thesis were: (1) to obtain information on the following questions: Are there any phosphorus compounds that can be applied at high enough concentrations, are absorbed well, and are sufficiently available for plant metabolism to contribute significantly to the phosphorus requirement of plants? (2) develop a technique which would permit quantitative screening of a large number of compounds with respect to their suitability as phosphorus sources for application to leaves; (3) determine quantitatively how well new compounds are absorbed and translocated out of the treated area; (4) determine whether any yield response can be obtained by using these compounds in treatments in field experiments; (5) evaluate some factors which are thought to be most important in affecting foliar absorption. It was considered that the information obtained in these investigations should contribute to the generation of new research on the practical aspects of foliar application of phosphorus.

II. LITERATURE REVIEW

Certain aquatic plants such as species of Elodea, Lemma, and other Vallisneria absorb most nutrients through their submerged leaves. The leaves of these plants do not contain stomates and are not covered with cuticle. Absorption occurs directly into the cells. In terrestrial plants, a waxy cuticle is formed on the outer epidermal walls of the stems and leaves; yet they too can absorb salts applied to their leaf surfaces. Wittwer (1964) pointed out that present-day terrestrial plants during their evolutionary development from their origin in the oceans never lost their ability to absorb nutrients and water through their aerial parts.

The foliar application of micronutrients including iron, zinc, manganese, boron, copper, and molybdenum has been a commercial agricultural practice for several decades. Gris discovered in 1844 that a chlorotic condition observed with plants on calcareous soils could be overcome by applying solutions of iron salts to the leaves.

With respect to the macronutrients, the greatest success has been achieved with nitrogen. Urea is absorbed very well and can be applied in quantities great enough to contribute to the crop requirement for nitrogen. For example, 80 percent of the total nitrogen applied to Hawaiian pineapple fields is applied to the foliage as urea sprays (Wittwer et al., 1963). Boynton (1954) wrote the first review on foliar absorption.

Much of the work done in this country has been reviewed by Wittwer (1957), Wittwer and Teubner (1959), Tukey et al. (1956, 1961), Biddulph (1960), Tukey et al. (1962), Wittwer (1964), Jyung and Wittwer (1965), Wittwer et al. (1965), Wittwer and Bukovac (1969), Wittwer et al. (1962a, 1963), Gray and Rose (1968) and Van Wazer (1958). Reviews by English authors include those by Halliday (1961) and Thorne (1954b, 1955a). Research done in Europe and Eastern European countries on the subject of foliar feeding was summarized by Burghardt (1961, 1964). Krzysch (1958a), Ferencz (1963) and Beeftink et al. (1957). Over the years there has been about as much research on foliar application of phosphorus as on foliar application of nitrogen. Reviews emphasizing the application of phosphorus have been written by Silberstein and Wittwer (1951) and Krzysch (1958b).

A. Feasibility of Foliar Applications of Phosphorus

Biddulph (1941) was one of the pioneers employing P^{32} to prove that bean plants can translocate injected radiophosphorus. Yatazawa and Higashino (1952a) established that radioactive phosphorus easily penetrates the epidermis of sunflower leaves and that flowers and flowerbuds especially seem to accumulate radioactive phosphorus. Kick and Hellwig (1959) found that sunflowers could be completely supplied with nitrogen, phosphorus, and potassium through foliar application. Phosphorus was supplied as a 1% glycerophosphate solution. Aufhammer and Hopfengart (1952) found that immersing barley seedlings every third or fourth night in phosphorus nutrient solution was sufficient to prevent any visible deficiency symptoms. The entire phosphorus requirement of sugar cane may be supplied by foliar application of KH_2PO_4 according to Burr et al. (1956) and Burr (1962). Wittwer and Lundahl (1951) used autoradiography to determine that phosphorus was absorbed by the leaves of a wide variety of crops and was translocated within a few hours to all parts of the plants, particularly the meristematic regions. Tukey et al. (1952) found that foliage feeding must take into account other portions of the plant such as trunk, branches, and shoots, as well as the foliage. Wittwer (1951) found that one to five sprays of 0.3% orthophosphoric acid applied during early fruit growth supplied 70 to 80 percent of the total phosphorus mobilized into the tomato fruits. In the same paper, he observed that the application of nutrient to the leaves of plants would likely have its greatest merit as a means of supplementing the supply of nutrients ordinarily absorbed by the roots.

Ishihara (1958) found that orange trees three to four years old grew better when sprayed with $(NH_4)_2HPO_4$ and that the phosphorus content of the leaves, the fruit size, and the fruit weight were increased. Under conditions of phosphorus deficiency, however, he did not succeed in applying enough phosphorus by foliar spraying to meet the needs of the plants. Tueva et al. (1962) claimed the same for squash.

B. Pathways and Mechanisms for Entry into the Leaves

Absorption of nutrients by leaves is a multistep process. Franke (1967) considered that the overall process of foliar absorption takes place in three stages. In the first stage, substances supplied to the surface of leaves penetrate the cuticle and the cellulose wall via limited or free diffusion. In the second stage, these substances, having penetrated the free space, are adsorbed to the surface of the plasma membrane by some form of binding, while in the third stage, the adsorbed substances are taken up into the cytoplasm in a process requiring metabolically derived energy. Franke concluded that, as a rule, for substances to be absorbed by leaves, in contrast to roots, they first have to penetrate the cuticle, a lipid-like layer. Another good review dealing with the mechanism of phosphorus absorption is written by Yatazawa (1954).

Until recently it was thought that the cuticle was the biggest obstacle, and that the absorption took place mainly through the stomatal pores. However, the passage through stomatal pores has only the effect that solutions enter cavities (Franke, 1967) such as stomatal chambers and intercellular spaces but not the cells themselves. Since the outer walls of cells lining these cavities are also covered by an internal cuticle, the problem is merely shifted from the outer to the inner surface of the leaves. According to Boynton (1954), uptake probably occurs through both cuticle and stomata.

The greatest natural penetration of water-soluble substances occurs through the anticlinal epidermal cell walls, the same walls through which the transpiration stream moves (Currier and Dybing, 1959).

1. <u>Cuticular membranes</u>

Diffusion through cuticular membranes is relatively rapid, as demonstrated by Wittwer et al. (1965) by using enzymically separated cuticular membranes.

Cations (potassium, calcium, magnesium) penetrate cuticles more readily than anions (phosphate, sulfate). The rate of absorption of urea exceeds that of cations by 10- to 20-fold. Movement into the leaf through the cuticle is greater than the movement out (Yamada et al., 1964b).

The rapid diffusion of urea through cuticular membranes is most significant. This may explain in part why urea is so effective as a nutrient spray for nitrogen. Urea not only permeates cuticular membranes far more readily than do nutrient ions, but the rate also increases with time (Yamada et al., 1965). Once cuticular entry is effected, solutes may be either absorbed directly by leaf cells or transported by diffusion within a free-space volume.

Leaf hairs usually have thinner cell walls or less cuticularization near their bases and are usually relatively effective in nutrient uptake (Linskens et al., 1965; Woolley, 1961).

2. The cell wall

The second barrier is formed by the cell wall, which is penetrated by a multitude of small strands designated as ectodesmata. Plasmodesmata, in turn, interconnect all living cells, in this sense making the protoplasm of the entire plant an organic whole. Many of the ectodesmata penetrate the outer wall of the epidermis and terminate beneath the cuticle. The location and frequency of these ectodesmata probably are related to the phenomenon of foliar absorption.

Preferential pathways for absorption through the leaf surfaces include epidermal cells and stomatal guard cell walls. From an exhaustive review of the literature and evidence cited from his numerous experiments, Franke (1967) has shown that these loci are consistently equipped with the greatest number of ectodesmata. Moreover, turgid leaves contain more ectodesmata than wilted leaves, and the number is much greater during the night and early morning than during the daytime hours. Furthermore, foliar absorption is generally known to be favored where stomata exist or occur in large numbers. Ectodesmata likewise occur regularly and in large numbers in and around the stomatal guard cells.

3. The plasma membrane

The third barrier is the plasma membrane. The membrane is permeable only for water, and it is therefore called semipermeable. The penetration of other compounds is the subject of many theories and is even less understood than that through the cuticle or the cellulose wall. Depending upon the nature of the molecule and the time it reaches this membrane, it may or may not gain entry to the living symplast.

4. Mechanism of foliar penetration

The cuticle appears to be penetrable principally via intermolecular spaces. The frequency of fissures, breaks, and punctures is certainly not so great that these openings allow a mass flow, although they may sometimes facilitate penetration. From the kinetics of the appearance of penetrated substances in the pure water chamber in experiments with isolated cuticles, it appears that the movement of ions and organic compounds occurs by diffusion. The experimental results fit a mathematical equation derived from theoretical considerations of diffusion. Cations penetrate the cuticle more rapidly through intermolecular spaces of cutin than do anions, which are hampered by the negative charges of the cuticle. Similarly, nonpolar undissociated molecules (urea) enter even more readily than cations. Urea penetrates the cuticular membrane with a velocity higher than one would expect from simple diffusion (Yamada et al., 1965). The kinetics of urea penetration are remarkably different from those of other substances. The extent of the penetration exceeds that of ions by 10- to 20-fold and is independent of the concentration. This increased permeability for urea also favors foliar absorption of ions, such as iron and phosphate, which are applied together with urea to bean plants, citrus, and pineapple. Yamada et al. (1965) concluded that the effect of urea on the cuticular permeability is based upon the loosening of the membrane structure by changing ester, ether, and diether bonds between the macromolecules of cutin.

According to Bukovac and Morris (1968), the mechanism of penetration through the cell wall must be diffusion. There seems to be different paths for lipophilic substances, and the hydrophilic solutes, which follow the spaces filled with water or aqueous solutions.

Incorporation of penetrating substances into the protoplast is the decisive step of absorption and occurs along the surface of the plasma membrane or at particular sites on it. It is an energy-requiring process and depends on the metabolic processes. There are several theories in the literature about the mechanism of active absorption, such as the carrier theory, change of permeability, and pinocytosis. It would lead us too far from our subject to go into those details.

Translocation of the absorbed material to other areas of the leaves or to other plant parts takes place regularly. It is thought to occur via plasmodesmata (symplast and phloem) and will not be dealt with here.

Dybing and Currier (1961) measured a significant cuticular penetration of P^{32} phosphate. They also remarked that surfactants vary in their ability to promote stomatal entry and that the concentration of surfactant necessary for stomatal penetration varied with the species being tested.

Yamada et al. (1964b) found that the cuticular membranes are highly permeable to monovalent and divalent cations and anions. Penetration occurs equally well through cuticles from plant surfaces with or without stomata. Furthermore, absorption occurs more readily than leaching. Their data suggested that uptake dominates loss of nutrients through foliar surfaces. The rate of penetration through different cuticular surfaces was directly related to the extent of ion-binding on the surface which was opposite the site of initial entry. It is possible that the greater ion-binding on the inside compared to the outside of isolated cuticular membranes facilitates foliar absorption. Okuda and Yamada (1962) found that lipid solubility is one of the important factors controlling the penetration of phosphoric acid through the leaf surface. Organic compounds like butyl alcohol and urea, which are rather soluble in lipids, increased the uptake of phosphorus when applied with the spray to the leaves.

Ahlgren and Sudia (1967) found that phosphate uptake is an active process and is energy dependent. Thus it is not surprising that light increases phosphate uptake. The greater absorption by immature leaves is not due to fewer barriers (i.e., thinner cuticle) but is metabolically controlled and probably has an energy requirement.

5. Rate of uptake

Vogl (1960) measured an uptake of 57 to 69% of the applied 0.004 M H_3PO_4 within 30 days with spruce. Yung and Wittwer (1964) measured phosphorus absorption by primary leaves of bean plants at 0.78 micromoles per cm^2 per hour from a very dilute phosphoric acid solution at pH 3.5. They also concluded that phosphorus uptake through the leaves is a metabolic process, and they proposed that proteinaceous carriers play an important role in uptake.

Thorne (1958) measured a rate of uptake of P^{32} from labeled NaH_2PO_4 solutions sprayed onto one leaf of swedes or French beans. The uptake was rapid during the first few hours and fell to zero after 4 days. P^{32} was detected in the root after 3 hours and continued to move out of the treated leaf for at least 6 days after application. Burr (1962) measured 50% absorption of the applied phosphorus from KH_2PO_4 within 15 days on sugar cane. Wittwer et al. (1963) listed the time required for 50% absorption as 6 days for beans, and 7 to 11 days for apple.

Sosa-Bourdouil and Lecat (1957) found that the P penetration greatly varied with different plant species and increased with the time of contact.

6. Translocation

Biddulph (1941) showed that phosphorus migration and the distribution throughout the plant of radiophosphorus injected into bean leaves varied throughout the day. The initial translocation was predominantly downward. The greatest downward movement was in the morning, and maximum upward translocation was near noon, but the amount was small. He thought that a mechanism existed whereby a daily periodic circulation of phosphorus may take place within the plant. Barinov (1959) applied the double labeled compound $Ca^{45}(H_2P^{32}O_4)_2$ to tomato plants and studied the comparative rates of absorption and translocation of both elements. He concluded that the entry of salt following foliar application can take place in ionic as well as molecular form. The movement of P^{32} or Ca^{45} in the plant is relative and determined by the physiological condition of the plant or of the individual part or organ of the plant. Barinov found that the movement of Ca^{45} was 1.3 to 2 times less than the movement of P^{32}. Calcium and phosphorus both move upward and downward and may be translocated to the roots.

Uturgauri and Oniani (1963) found that P^{32} appeared in the roots of tea and corn plants within 24 hours after application when there was a shortage of mineral nutrients in the soil. Eynard (1961a, 1962, 1964) measured significant translocation of phosphorus in seedlings of olive and citrus trees.

Barrier and Loomis (1957) found that 15% of the radioactive phosphorus applied to soybean leaves was absorbed in 2 hours, and 34% of the absorbed phosphorus was eventually translocated out of the treated area to all parts of the plant, including the roots. Eighty percent of the absorbed P^{32} was present in organic form after 24 hours. More than 2 hours was needed for translocation of significant quantities of P^{32}, and the translocation was slowed or stopped by depletion of leaf carbohydrates. Radioactive photosynthate may move out of soybean leaves within minutes after supplying $C^{14}O_2$. This difference suggests that chemical or physical transformation is required before P^{32} can be translocated through the phloem of soybean plants. Barrier and Loomis found also that 6 hours after painting leaf blades of beets with P^{32} solution, a large percentage of the phosphorus was concentrated in the veins. This loading of the veins occurred in the absence of translocation from the blade but required a supply of available carbohydrate.

Moustafa et al. (1971) reported excellent translocation of foliar applied phosphorus to leguminous root nodules and found that 50% of the radioactivity was in ATP, ADP, and AMP, and more than 90% of the P^{32} was localized in the soluble part of the plant tissue of the nodules.

Colwell (1942) found in studies on the rate and direction of transport and uptake that the localization of radioactive phosphorus under various conditions showed that when this indicator is restricted to the phloem, its movement is correlated with food movement in the plant.

Autoradiographs by Biddulph (1956) showed that P^{32} introduced into red kidney bean plants through the leaflet injection method moves downward principally in the phloem of the vascular traces from the treated leaf. Where the activity was the heaviest, there was some lateral movement through living cells to the xylem. Marshall and Wardlaw (1973) found that the movement of phosphate from leaves is largely determined by the movement and demand for carbohydrate within the plant and not by the phosphorus requirement of the sink. Linck and Swanson (1959) concluded that translocation of absorbed phosphorus by the leaves of peas is very much dominated by the development of the flower and the pod of the node.

Kendall (1955) found that the translocation of P^{32} was inhibited when dinitrophenol or sodium fluoride was placed in the vicinity of the phloem cells through which the transport occurred.

7. Leaching of phosphorus

Tukey et al. (1958a, 1958b, 1965), Tukey and Morgan (1964), Tukey and Tukey (1969), and Emmert (1961) found that phosphorus is a difficultly leachable element. They found that nutrient losses by leaching from very young leaves were very small but increased with leaf maturity and were largest as leaves approached senescence. Losses from phosphorus-deficient plants were 1.5% of the P^{32} in the leaves, whereas from the plants grown at the normal phosphate level only 0.09% of the P^{32} of the leaves was removed. Losses were greater from older leaves than from young leaves, varied with the type and nature of the plant, and increased with the duration of the leaching. Leaves attached to the parent plant can lose several times as much nutrient as is contained at any one time in the leaves, indicating the existence of a replenishment mechanism.

Emmert (1959) found that loss from the roots of foliar applied P^{32} occurred as an exponential function of ambiant phosphorus concentration. Loss to demineralized water was greater than loss to tap water.

Eggert et al. (1952) found in field experiments with 25-year-old apple trees that 3.71 inches of rain in 6 weeks between spraying and analysis only caused very small losses from washing off by rain.

C. Techniques for Measuring the Uptake of Nutrients through Leaf Surfaces

Boynton (1954) reviewed the early progress in nutrition by foliar application and techniques used to measure response. Many crop plants have been sprayed with iron to eliminate calcium- or manganese-induced chlorosis. Sprays of soluble salts of zinc, manganese, copper, boron, and molybdenum have also been extensively used, the index of absorption being the correction or prevention of specific nutrional disorders apparent on the foliage or the fruit.

The value of urea nitrogen applications in apple orchards (Boynton, 1954) was first determined by increases in leaf chlorophyll, total leaf nitrogen, and productivity. Leaf sprays were as effective, or possibly more so, than applications of the same amount of nitrogen to the soil.

In addition to visual color differences, correction of other specific disorders, growth responses, and changes in mineral content, radioactive isotopes and certain stable isotopes differing in mass, offer a unique and sensitive way to measure the absorption of nutrients applied to plant surfaces.

One of the first considerations in studies of foliar absorption of labeled mineral nutritions was where and how the treating solutions are to be applied. Perhaps the earliest reports in which radio-phosphorus was utilized in studies of leaf absorption and subsequent transport were those of Biddulph (1941) and Colwell (1942). Both used radiophosphorus and special leaf injection for infiltration techniques as a means of introducing the nutrient. These papers established the free mobility and rapid movement within the plant phloem of phosphorus abosrbed by the leaves. With radioactive isotopes, foliar absorption rates and distribution patterns may be precisely established, and foliar absorbed nutrients may be distinguished from those which are absorbed through the roots or are already present in the plant. Furthermore, the extent of the nutrient contribution from foliar sprays may be accurately assessed.

Beginning in 1950, numerous papers appeared portraying the rapidity of transport and the pattern of distribution, and giving an evaluation of the nutritional condition of P^{32}-labeled phosphates applied to the leaves. Silberstein and Wittwer (1951), and Wittwer and Lundahl (1951) established that radioactive phosphorus is rapidly absorbed by the leaves of tomato, corn, bean, and squash plants and translocated to the root tips and other centers of high metabolic activity. Within 48 hours after treatment, 5 to 6% of the total phosphorus in developing tomato fruit may be derived from a single foliar application of a 25 mM solution of orthophosphoric acid. Also approximately 20% of the increment of phosphate uptake in the fruit between 8 and 20 hours after treatment was derived from that absorbed through the leaves. Similar results were obtained by Eggert et al. (1952) with apple trees. From 2 to 3% of the phosphorus in the plant came from a single foliar spray within 30 days of application. Over half of the absorbed phosphate was translocated to the roots. The efficiency of utilization of the applied phosphate was apparently very high and approached 100% after prolonged absorption. All authors used the method of measuring the absorption of radiophosphorus by several crops following momentary dipping of single leaves or spraying the foliage and subsequently assaying the accumulation of radioactivity in non-treated plant parts such as the roots. Distribution in the plant was followed by gross autoradiography (Wittwer and Lundahl, 1951).

The leaf-dipping and spraying techniques were not very quantitative for measuring the absorption and translocation of phosphorus. A closer approximation of absorption rates may be obtained by applying the isotopically labeled nutrient as droplets onto the surface of bean leaves and removing the disc containing the nonabsorbed residue. Values obtained with this method are underestimates, like the ones obtained with the leaf-dipping and spraying techniques, because the absorbed nutrients in the leaf disc itself are not included. However, Bukovac and Wittwer (1957) used the leaf-disc removal technique to obtain values both for foliar absorption and mobility in the bean plant.

Jyung and Wittwer (1965) outlined and reviewed a more accurate technique for measuring absorption of isotopically labeled nutrients applied to limited areas on leaf surfaces. In this technique, the treatment site is washed, according to standardized conditions after a given interval of absorption, with distilled water or some complexing agent.

Bukovac and Wittwer (1961) concluded that, of the several techniques utilized for studying foliar absorption of labeled mineral nutrients, the leaf-washing procedure offered the most promise for accurately distinguishing between the absorbed and nonabsorbed nutrients following application to leaf surfaces, for minimizing errors encountered with some nutrients that are not readily translocated, and for accurately establishing absorption rates.

Van den Hende et al. (1960) and Van Cleemput and Van den Hende (1965) developed a technique to apply known quantities of phosphorus so to study its absorption by means of wetting pieces of tissue paper on the leaf surface.

Burr et al. (1956, 1958) made extensive use of P^{32} to study the absorption of phosphorus by sugar cane leaves and the circulation of phosphorus in the sugar cane plant.

The development of the leaf immersion and washing technique is very important in the studies of environmental influences on phosphorus absorption. Intact primary leaves of the bean or other convenient plant materials are immersed in a labeled nutrient solution for various time intervals, and the leaves are then washed and blotted. Absorption is expressed as the amount taken up per unit time from a known concentration in an external solution maintained under standard conditions of light, temperature, and oxygen tension. This treating procedure was designated by Jyung and Wittwer (1964) as the leaf-immersion and leaf-washing technique and the measurement of foliar uptake as "specific absorption".

D. Phosphorus Sources

Silberstein and Wittwer (1951) tested various organic and inorganic phosphorus compounds on vegetable crops by applying four weekly foliar applications of the solutions at concentrations of 25 to 100 milimoles of phosphorus per liter. Most compounds were not injurious to foliage at 50 milimoles per liter, but some were. They concluded that the inorganic phosphorus compounds were generally better than the organic ones. Orthophosphoric acid was generally the most effective of all the chemicals used for foliar application. The organic phosphorus compounds tested included glycerophosphoric acid, sodium glycerophosphate, ethyl acid phosphate, methyl acid phosphate, potassium glycerophosphate, magnesium glycerophosphate, a nitrogen-bearing propyl acid phosphate, a nitrogen-bearing butyl acid phosphate, ethyl triethanolamine phosphate, fructose 1-6 diphosphate, tetraphosphoglucosate, and calcium glycerophosphate.

Naundorf (1951) reported that sand-cultured lettuce seedlings sprayed with a solution of 2.5 to 10 grams of calcium glycerophosphate per liter grew as well as, or slightly better than, those provided with KH_2PO_4 in the Knop's solution. Tomato seedlings sprayed with a solution of 10 grams of calcium glycerophosphate per liter showed marked superiority over those supplied with complete Knop's solution.

T'yuki et al. (1957) reported that bean leaves sprayed with solutions of different phosphates at pH 2 to 5 absorbed phosphorus in the following decreasing order: NH_4-phosphates, Na-phosphates, K-phosphates.

Krzysch (1958b) found in tests with phosphorus sprays on oats and bush beans that various solutions showed the following decreasing order of efficiency: $Mg(H_2PO_4)_2$, superphosphate, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, and KH_2PO_4.

Okuda et al. (1960) measured the translocation of various sources of phosphorus and found that translocation of applied phosphorus was greatest with urea phosphate. Calcium and ammonium phosphate proved to be similar.

Burghardt (1961) concluded in his review that the results obtained with various phosphorus sources such as superphosphate and monobasic orthophosphates of magnesium, potassium, and ammonium depend on the different plant types.

Datta and Vyas (1967) concluded that ammonium phosphate and superphosphate were absorbed up to 41% within 7 days after application, whereas the absorption from mono- and dicalcium phosphate was only 31% in the same time.

Eggert et al. (1952) found in greenhouse experiments on one-year-old apple trees that diammonium phosphate was absorbed to a greater extent than were monoammonium phosphate, disodium phosphate, trisodium phosphate, or monocalcium phosphate. Fisher and Walker (1955) found that the rate of intake of phosphorus by apple leaves was greatest with phosphoric acid, slowest with $Mg(H_2PO_4)_2$, and intermediate with $NH_4H_2PO_4$ and KH_2PO_4. Tormann et al. (1969) measured the phosphorus uptake from single leaves of apple trees dipped in different phosphorus-bearing solutions. Absorption of phosphorus was better from phosphoric acid and monoammonium and potassium phosphates than from monocalcium phosphate.

Coic et al. (1965a, 1965b) found that maize and tomato plants deficient in phosphorus rapidly absorbed tripolyphosphate and pyrophosphate, as well as orthophosphate, through their roots. Absorption of "soluble" metaphosphate or co-called long-chain polyphosphate was not demonstrated. Conesa (1969) found in experiments with potatoes that, although orthophosphate was absorbed preferentially, polyphosphates were also absorbed directly, without preliminary hydrolysis. Roux (1968) reported that barley roots absorbed phosphorus as orthophosphate from nutrient solutions containing condensed polyphosphates. These were adsorbed on the root tissue and, on hydrolysis, orthophosphate and possibly oligo-phosphates were absorbed. Tsuge and Yoshida (1958) reported that, under waterlogged conditions, polyphosphates produced greater rice yields than did superphosphate, and their residual effect on naked barley was greater. Generally, polyphosphate with a ring structure was more favorable for growth and yield of crops than was polyphosphate with a chain structure. The available phosphorus from polyphosphate was though to be ortho-phosphoric acid produced by hydrolysis. Sutton and Larsen (1964) found that the hydrolysis of pyrophosphate in soil was largely an enzymatic process and that, in soils with unimpeded activity, pyrophosphate will not persist long enough for differences between ortho- and pyrophosphates to affect phosphorus uptake and the growth of plants.

E. Crop Response to Foliar Applications of Phosphorus

Sugar cane: De Datta and Moomaw (1965) found that young sugar cane plants grown on strongly phosphorus-fixing soils responded significantly to four foliar sprays in which 169 milligrams of phosphorus per pot, containing 2 plants, were applied. Phosphorus was applied either as $NH_4H_2PO_4$, $K_4P_2O_7$, or superphosphate. Foliar spraying greatly increased plant phosphorus, and the level was 20 times greater when $NH_4H_2PO_4$ was applied to the leaves rather than to the soil, but the extra phosphorus was not necessarily translocated or involved in metabolism. Burr et al. (1958) found that the lower leaf surface of sugar cane absorbs more efficiently than the upper. Ammonium phosphate was absorbed more readily than the potassium salt. The total absorption leveled off at about 125 micrograms of phosphorus per cm^2 of leaf surface. Sugar cane translocates the phosphorus from one stalk to another, as indicated by the fact that 32% of the P^{32} of a labeled ammonium phosphate solution absorbed from a foliar application of phosphorus to one stalk was found in other stalks 12 days later. The Hawaiian Sugar Planters Association (1951) reported that 75% of the phosphorus applied as potassium acid phosphate was absorbed within 30 days after application. Carpenter (1961) reported the results of several experiments in which sprays of monopotassium phosphate and monoammonium phosphate on sugar cane raised the sugar content by 10% and improved the juice quality. Cresp (1964) reported that yields were increased by aerial application of 15 pounds of phosphate per acre to plant cane. Best results were reported with spraying with monoammonium phosphate 20 to 40 days before cutting.

Sugar beets: Yakuskin and Edelshtein (1952) reported that spraying with phosphorus-bearing solutions increased the sugar content of beets in field experiments and under commercial conditions. Best results were obtained with a 5% solution applied at the rate of 800 liters per hectare. Yakushkina (1960) reported that spraying two or three times with NH_4NO_3 or superphosphate during the vegetative period accelerated growth but did not always increase root yield. It was found that spraying increased the translocation of sugars to the roots. Sommer (1964) found that spraying with a 2.5% superphosphate solution on September 29, 5 weeks before harvesting, did not result in a significant yield increase except with the "Plenta" variety. Bakermans (1957) measured a slight increase in beet yield when sugar beets were sprayed 2 to 4 weeks before harvest with a dilute superphosphate solution. Rid (1964) measured an average of 9% extra yield over 6 years of experiments in spraying sugar beets on calcareous and humus soils with 40 kilograms of P_2O_5 equivalent per acre. Yield increases were greater in dry years than in normal or wet years.

Potato: Rid (1964) in Germany sprayed potatoes with a superphosphate solution in the quantity of 20 kilograms of P_2O_5 equivalent per hectare just before closing of the stand

and reported yield increases of 9% over an average of 6 years. Bakermans (1957) reported an increase of the underwater weight of potato tubers when the foliage was sprayed 4 to 8 weeks and 2 to 4 weeks before harvesting. The most effective time of foliar application of phosphorus was spraying them 5 weeks before harvesting. Laughlin (1962) found that spraying potato plants with NaH_2PO_4 solutions tended to increase the dry matter and phosphorus content of the tubers and to decrease the nitrogen content. Krzysch (1958c) found that six sprays of a 2% KH_2PO_4 solution on potatoes during the first few weeks of growth hastened maturity and increased dry matter yields.

Wheat: Shereverya (1960) found that, in pot experiments with wheat, P^{32} applied to leaves appeared in large amounts in the grain, but the total phosphorus content of the shoot and particularly of the grain was not always increased and was sometimes even decreased. Ferencz (1954) reported a slight increase in yield after several sprays of a 5% superphosphate solution. Rozhanovskii (1956) reported an increase in yield of wheat of 13 and 15.3 quintals per hectare after spraying with superphosphate solution. It was also found that dusting with superphosphate was less effective than spraying. Suleimanov (1956) reported that a 5% superphosphate solution increased wheat yields by 7 to 12% on sod-podzolic soils. The phosphorus content of the grain was raised by 0.02% compared with the controls.

Clover: Suleimanov (1956) reported an increase in the phosphorus content of clover leaves sprayed with superphosphate solution. Labeled phosphorus absorbed by the leaves was found in the roots after 7 hours. Singh and Pandey (1969) reported an average increase in yield of 2.7 quintals of Egyptian clover seed per hectare after spraying with 2.5 quintals of superphosphate per thousand liters per hectare. The quality of the seed was also significantly improved. Bouma (1969) was less successful with spraying subterranean clover grown on minus-phosphorus solutions in river sand. The plants were sprayed once every 2 or 3 days with a 0.1% phosphorus solution. The dry weight of the sprayed plants was no more than 40% of that in the control treatment receiving root phosphorus. He found further that 7 days after application of a tracer solution the treated leaflet of the first and fourth trifoliate leaves still contained 77 or 70% of the amount absorbed by the plant. Relatively slow rates of uptake of phosphorus applied to the leaves were considered at least partly responsible for the poor growth responses compared with phosphorus applied to the roots. Campbell (1956) could not see any visual difference after spraying 25 kg of diammonium phosphate per hectare on hill-country pastures.

Cotton: Lancaster and Savatli (1965) reported that, where phosphorus deficiency existed, foliar application of phosphorus to cotton at frequent intervals during fruiting increased the yield, but not beyond that obtainable by soil application alone. Under slight to moderate phosphorus deficiency, foliar feeding was effective in correcting it. Earliness of cotton, although markedly increased by soil application of phosphorus where a large yield increase occurred, was little affected by foliar application of phosphorus and only under severe phosphorus deficiency. Late season foliar applications may correct slight phosphorus deficiency, but application early in the fruiting period is necessary to correct even moderate deficiency. Use of dilute phosphorus solutions was necessary to avoid leaf injury; even solutions containing 1.5% P_2O_5 equivalent caused some leaf injury. Bhoj et al. (1969) recorded a significant increase in yield of cotton in a pot experiment after spraying twice with a 0.2% solution of phosphate as KH_2PO_4. Verma and Sahni (1963) also reported yield increases due to phosphorus sprays.

Grapes: Pecznik (1959, 1962, 1964) reported increases of grape yields by 18 to 33% after spraying with a 2% superphosphate solution. The sugar content of the grapes was also increased. There was a significant negative correlation between the efficiency of foliar sprays and the age of the vineyard. Ishihara et al. (1966) reported that spraying mature vines with potassium monophosphate increased their vigor and led to earlier shoot ripening, greater bunch weight, and better berry quality. The phosphorus content of the various parts of the vine was increased. A 28.1% increase in the phosphorus content of the leaf petioles was observed. Spraying young vines increased shoot diamter, leaf size, and number of flower clusters. Leaf color and root development was enhanced. The yield per vine, average bunch weight, and number of berries per bunch were also increased. Berry color was improved, and the free acid content of the juice was reduced. Arzumanov (1966) found that spraying with 1% potassium phosphate at the beginning and again at the end of July increased bunch size and sugar content of the berries, advanced the harvesting date, and improved shoot maturity and structure both in the same year and in the year following the application. Arhangel'skaja (1960) reported on experiments with vines which had superphosphate solution applied to the roots in comparison with vines to which the superphosphate was applied to the foliage and with others where phosphate smoke was generated by igniting red phosphorus under the vine. Foliar fertilization resulted in poor growth and fruit low in sugar. Root nutrition and smoking both resulted in good growth of the vines, provided that the smoked vines were either enclosed during the treatment or sprayed with water. Smoke treatment resulted in the highest yield of fruit, and the grapes produced upon these vines had the highest sugar content. Cook et al. (1968) measured neither a significant increase in fruit yield from phosphorus spray nor an increase in phosphorus content of the foliage.

<u>Tomatoes</u>: Tatsumi and Kageyama (1964) reported that sprays of phosphorus were very effective on tomato seedlings

in the later stage of growth. The ability to develop new roots and to absorb minerals was influenced by foliar spraying with phosphorus-bearing solutions in the early growth stage. The seedling quality was especially strongly influenced by phosphorus sprays on a rich fertilized nursery soil. Silberstein and Wittwer (1951) found that, within 48 hours after treatment, 5 to 6% of the total phosphorus in developing tomato fruit may be derived from a single foliar application of a 25 mM solution of orthophosphoric acid. Beeftink et al. (1957) reported that sprays of 0.2% orthophosphoric acid or a 0.4% solution of double superphosphate on tomatoes grown in poor soil can improve the pollination and earliness of the yield. Similar results could also be obtained by adding sufficient phosphorus to the soil. Pudelski (1959) reported that spraying was as effective as soil application in promoting the yield and development of tomatoes. Fruit composition, however, was particularly affected by spraying shortly before maturing of the fruit. Hernando and Sanchez Conde (1966) found that monopotassium phosphate was a good phosphorus source for tomatoes when applied to the leaves. Bottini and Morra di Lavriano (1958) reported that tomato growth was more than doubled by sprays of 0.06% $(NH_4)_2HPO_4$. The efficiency of this spray was increased by the addition of 0.065 ppm of zinc. Both sprays were applied to the potted plants twice weekly, altogether 15 times.

Beans: Bukovac and Wittwer (1957) found good absorption of phosphorus applied to bean leaves. Krzysch (1958b) found that a foliar spray of 0.35% phosphorus and soil application of phosphorus gave similar bean yields. Gorski and Sokol (1962) found that, in beans grown in water culture, the application of labeled H_3PO_4 solution to the leaflets resulted in 70% uptake of phosphorus, from which only about 2% was translocated in the direction of the roots.

Fruit trees: Sato et al. (1954) found that six to eight sprays of 1% monoammonium phosphate solution increased the growth of peach, pear, grape, and orange seedling trees over the nonsprayed controls. Eggert et al. (1952) found in field and greenhouse experiments that water-soluble radioactive phosphorus salts applied as spray to leaves and small branches of apple trees could be absorbed and translocated to other parts of the trees.

Diammonium phosphate was absorbed to a greater extent by one-year-old trees in the greenhouse than were monoammonium phosphate, disodium phosphate, trisodium phosphate, or monocalcium phosphate. Kessler (1965) found it possible to reduce the amount of blossom shattering in grapes by a combination of zinc and phosphorus foliage spray. A heavier fruit set occurred on citrus trees. Krivko (1966b) reported an increase in sugar content of plum after three foliar applications of phosphorus. Pant and Singh (1971) found that a phosphorus spray of 0.2 or 0.4% dihydrogen phosphate on Red Delicious apples did not evoke any increase in phosphorus content in the leaves. The length-breadth ratio of the fruit was appreciably reduced by the phosphorus spray, and the ascorbic acid content of the fruit diminished, as compared with the control.

Soybeans: Belikov and Thatschenko (1961) and Belikov and Burtseva (1966, 1967) showed, by means of ^{32}P, that soybeans absorb phosphorus from superphosphate applied to the leaves as a solution or dust. A 2% superphosphate solution was sprayed on the leaves at the rate of 2 kg of phosphorus per hectare at the end of flowering on the assumption that this is a critical period for grain production. The yield was raised by 15 to 20%; seed size was increased 9%; the protein content of the seed, by 0.3%; and total oil production, by 16.6%. Singh and Singh (1968) confirmed the findings of Belikov and Burtseva. Burtseva (1967) found an increase in linoleic acid content of the seed as a result of spraying with superphosphate solution.

Tobacco: Oikawa et al. (1958) found that Calgon (the main component of which is sodium hexametaphosphate) increased the growth and is thought to be a suitable compound for supplementary foliar application of phosphorus on tobacco, while Hristozov (1965) found that when 50% of the fertilizer was applied to the soil and 50% was applied in one, two, or three foliar sprays, the yield increase was 14 to 18%.

Vegetable crops: Brasher et al. (1953) did not find any significant increase in yield resulting from nutrient sprays, including phosphorus, when a standard soil application of fertilizer had been applied prior to planting the crop with tomatoes, lima beans, cantaloupe, or cucumber in a 4-year study. Yeh (1967) measured an absorption of 40 to 60% of applied phosphorus by Chinese cabbage and spinach within 24 hours after application. No difference in phosphorus absorption was observed from various sources, including H_3PO_4, NaH_2PO_4, and $NH_4H_2PO_4$. Geissler (1955) found that spinach was capable of absorbing phosphorus applied to the foliage. Kherde and Yawalker (1966) found that the foliar application of 44.8 kg of P_2O_5 equivalent as triple superphosphate per hectare in three sprays to peas 61, 71, and 81 days after planting tended to be better than soil application of the same amount, but no treatment significantly affected height, leaf area, dry weight, grain yield, or haulm yields. Roy and Seth (1970) reported good growth of radish and an increase in yield resulting from the application of half of the normal phosphorus addition through foliar application. McCall and Davis (1953) did not recommend phosphorus as a spray because they applied several sprays of orthophosphoric acid in the amount of 10 pounds of P_2O_5 equivalent per acre on onions and celery and did not increase the yield in one year and closely approached significance in reducing the yield another year. Norton and Wittwer (1963) found, in field studies with strawberries, significant yield increases from spring application of phosphate sprays when the level of phosphorus in the soil was low. Bondarenka and Parshikov (1961) measured an increase of 20% in hop strobiles after a series of four foliar applications of nitrogen and phosphorus. Sadaphal et al. (1968) increased the yield of groundnuts by 25 to 50% with sprays of superphosphate solution after a basal dressing of at least 20 kilograms P_2O_5 equivalent per hectare.

There are several reports on foliar application of phosphorus for ornamental crops. Stinson and Seeley (1960) found that soil application of phosphorus was more efficient in promoting linear growth of chrysanthemums than with foliar application. Seeley and Stinson (1964) found no essential differences in growth among plants receiving foliar application of 0.9% $NaH_2PO_4 \cdot H_2O$ made twice a week, once a week, or biweekly. The growth was significantly less than when the phosphorus was applied to the soil. Initially, the phosphorus sprays caused no leaf injury, but the same concentration applied many times in this experiment did cause leaf injury, which was progressively less from the base to the top of the plant, indicating that the injury was cumulative. Asen et al. (1953) found that 8% of the total phosphorus in the roots of chrysanthemum plants was derived from four successive foliar applications of a 0.3% solution of orthophosphoric acid within a 15-day period. The absorption of phosphorus applied to the leaves resulted also in an increase in dry weight of both the root and top portions of the plant. Sheehan et al. (1968) concluded that foliar fertilization would be effective for orchids, and Setlik and Trnkova (1957) obtained good absorption and translocation of P^{32} in detached geranium leaves.

Thümmler (1960) determined that larch and spruce would tolerate sprays with a maximum concentration of 1% of potassium or ammonium phosphate. Pine trees could be safely sprayed with potassium and ammonium phosphate at concentrations up to 5%. All these conifers showed good responses to foliar application of phosphorus. Schobmeyer (1961) briefly immersed the foliage of loblolly pine seedlings in 0.5 M $(NH_4)_2HPO_4$ and found that this treatment doubled the height growth of the seedlings in comparison with seedlings receiving no phosphorus, but this response was only 60% of that obtained with seedlings having 50 ppm of phosphorus available to the roots. Maximum quantities of P^{32} were found in root tips collected 48 hours after treatment. Five weeks after the foliar application of P^{32}, 65% of the phosphorus of new shoots was P^{32} which had been translocated from the foliar deposits on the older needles. Savina (1962) found that the phosphorus absorption by conifers varied among species (pine having the highest and larch the lowest absorption), plant parts, and times of application. Maximum absorption occurred in the "intensive" growth period.

The weight of maize cobs was increased by 18% after spraying the plants with superphosphate solution (Narayanan and Vasudevan, 1959). Pavlov and Ivanov (1960) reported that corn absorbed to a greater extent the phosphorus applied to the leaves when no nitrogen and potassium were applied to the soil than when they were applied.

Burghardt (1964) concluded his review by stating that the absorption of phosphorus applied to the leaves is accomplished very well by most plants, that the results depend on the plant type, and the MgH_2PO_4, $NH_4H_2PO_4$, and KH_2PO_4 are the best compounds. The maximum concentration tolerated by most plant species is 0.5%. One spray is usually not enough to contribute significantly to the phosphorus requirements of most crops. Hence, phosphorus spraying is not economically feasible for most crops under middle European conditions.

Additional research has been reported on the relationship between application of phosphorus-bearing sprays to the foliage. Lewis reported in 1936 that spraying lettuse daily for 5 weeks with a dilute solution of potassium phosphate produced a significant increase in phosphorus content of the leaves.

Kessler and Hewitt (1962) reported the results of their experiments on spraying tomatoes and fruit trees including apples, apricots, cherries, almonds, peaches, pears, plums, limes, lemons, oranges, and grapefruit. The phosphorus content of the terminal leaves reached peak values with 2 to 3 weeks following treatment and then gradually decreased. When foliar sprays of zinc and phosphate were applied together, the phosphate aided the movement of the zinc.

Terblanche et al. (1970) reported that an autumn spray of superphosphate increased the phosphorus status of the leaves but not of the spurs in apple trees.

Teubner et al. (1957) found that 12 to 14% of the total phosphorus in the parts of apple, cherry, corn, tomato, potato, and bean harvested for food could be supplied through multiple foliar sprays of 0.3% orthophosphoric acid. The percentage of the total phosphorus in these organs derived from foliar sprays was a linear function of the number of sprays applied. The accumulation in these organs of the radiophosphorus applied to the foliage was not reflected by a change in the total phosphorus, and the yields were not altered. It was concluded that phosphorus absorbed by foliage of plants grown in soil adequately supplied by phosphorus replaced, or was utilized in preference to, phosphate that otherwise would be absorbed by the roots from the soil.

F. Crop Responses to Complete Nutrient Sprays

There are numerous reports on the performance of complete nutrient sprays including nitrogen, phosphorus, and potassium and sometimes even calcium, magnesium, and micronutrients.

Sugar beets: Sugar beets appear to be very responsive to the foliar application of nutrients. Nagymihaly et al. (1954) found that sprays in late June and early July with 3% NPK solution hastened full maturity and increased the fresh weight of roots by up to 31%, the fresh weight of leaves by up to 33%, and the yield of sugar by up to 40%. Kuthy et al. (1952) recorded a 20% increase in yield of sugar beets and a 17%

increase in yield of sugar. Thorne (1955a) found that absorption of any of the nutrients tested from a spray containing more than one nutrient was unaffected by the presence of others in the spray, but spraying with solutions containing nitrogen increased the absorption of phosphorus and potassium from the soil, and potassium in sprays increased the uptake of phosphorus from the soil. The dry weight was increased by all three nutrients in the fertilizer, and the yield of sugar in the roots was increased by the sprays. Milica (1959) reported that the best results obtained from spraying the foliage with a complete NPK solution were an increase of up to 25.6% in root production, 35.4% in sugar yield, and 44.2% in leaf growth. The best time for spraying with phosphorus-bearing solutions was found to be 3 to 4 weeks before harvest.

Nagymihaly and Leszek (1963) and Milojic (1957) measured an increase in root yield but no increase in sugar content of beets after spraying with a complete NPK solution. Nagymihaly and Leszek noted that the great increase in ash and in the nitrogen and phosphorus content of roots and tops indicated that foliar sprays supplied nutrients and, in addition, stimulated nutrient uptake from the soil.

Davidescu et al. (1966) and Gruev (1966) both measured an increase in the sugar content but no increase in yield of beets after spraying with a complete NPK solution.

Small grains: Chumakov and Bystrova (1958) reported that, as a result of a combined spray of phosphorus and potassium in the spring on a background of fall and winter soil top dressing of winter wheat in field experiments, the infestation of leaves by leaf rust was reduced from 23.5% to 15.9%, and the grain yield was increased by 38%. Narayanan and Vasudevan (1957) measured an increase of 14.4% in grain yield as a result of a combined spray of urea and superphosphate. Davidescu and Davidescu (1960a) found the highest grain and straw yields and greatest number of fertile ears and grain per ear after five sprays of a 1% solution of NH_4NO_3 and superphosphate between the period of tillering and ear formation followed by a 3% solution of NPK. Von Boguslawski and Vömel (1957) obtained similar yields of oats as a result of adequate fertilization of the soil and spraying the plants with NPK solution in a pot experiment.

Tomatoes: Davidescu and Davidescu (1960b) obtained tomato yield increases of 3 to 17% (2-year average) after spraying three times between the time of flowering and fruiting with a solution of 0.5% nitrogen (NH_4NO_3), 1% phosphorus (superphosphate), 1% potassium (K_2SO_4), and 0.01% boron. Mel'nichuk (1960) reported that on podsolized chernozems the foliar nutrition of tomatoes with NP, NK, and PK solutions increased the yield by 30 to 39%; foliar nutrition with NPK solutions increased the yield by 15 to 48%. Windham (1965) reported that foliar sprays of NPK in addition to soil applications increased yields of greenhouse tomatoes. On the other hand, Mostert and Sonneveld (1964) reported that tomato plants adequately supplied with nitrogen, phosphorus, and potassium through the soil showed no yield response to foliar application of potassium nitrate, urea, or NPK fertilizer.

Grapes: Ch'in(1959) found that the cumulative weight of Concord grapes increased by 27% after foliar treatment with a 1% solution of superphosphate. The total sugar content improved by 5.5 to 27.8%, the highest value following NPK treatment. Derkunskaja (1961) found that the average bunch weight of grapes was increased by treatment with a solution of salts of phosphorus, potassium, and boron and that the sugar content of the berries was increased. Also, the wine quality improved. Damigella and Squillaci (1961) found that repeated sprays of an NPK solution had a significant effect on leaf size and on the sugar content of the juice but not on the yield of grapes. Prolonged application of these foliar sprays at brief intervals decreased the development. A well-balanced fertilizer was more beneficial than one high in nitrogen only. Aliev (1967) reported that net profits were increased due to increased yield and sugar content of the berries after foliar application of an NPK solution. The vegetative period was reduced by 10 to 14 days, and ripening was accelerated. Natali and Zucconi (1968) also reported a net gain in each of six vineyards after a soil application of nitrogen, phosphorus, and potassium in combination with application of five to nine sprays of urea with phosphoric acid and potassium sulfate during the growing season. The controls received the soil application only. The foliar nutrition increased fruit yields by an average of 22% and improved the quality of the fruit.

Tree and bush fruits: Il'inskij (1963) found over a 4-year period that apple, plum, and sour-cherry trees which produced moderate or poor blossoms benefited from sprays of 1.5 to 2% solution of NPK plus boron, zinc, and manganese at full bloom. Sprays of 2 to 3% NPK plus trace elements after flowering and again 2 to 3 weeks before harvest were recommended for all trees regardless of the amount of blossom. Ursulenko (1958) measured an increase in productivity of up to 32% due to an increase of photosynthesis during the first 10 to 15 days after foliar feeding with phosphorus and potassium on 20-year-old apple trees. Salmanov (1958) reported an average yield increase of 20% with black currant after foliar nutrition. Spraying with NPK at the end of August increased the number of flowers in the bud from 38.6 to 69%. McNall and Hinckley (1973) measured, as an average over 4 years, an increase of 19% in almond yield after spraying with a combination of zinc, manganese, and phosphorus. Enhanced yields were largely due to improved nut set and larger kernels.

Strawberries: Khodzhaeva (1961a, 1961b) reported that the highest yield increases with strawberries were obtained by spraying them with an NPK solution. Four-year-old plants responded more than two-year-old plants. Autumn spraying increased the number of berries, and spring spraying increased the berry size. Tognoni et al. (1968) measured highly significant yield increases after three sprayings of a 1 to 2% NPK solution. Earliness was not significantly affected by foliar nutrition.

Vegetables: Chen-Hsioh and Shu-Hsien (1957) reported increased tuber yield with sweet potatoes when fields deficient in phosphorus and potassium were sprayed with a solution containing these nutrients 1 to 2.5 months before harvest. The top growth was only slightly increased. Three applications at 15-day intervals were more effective than two. Kuthy (1954) reported that spraying lettuce seedlings with a 3 to 4% NPK solution resulted in nutrient utilization up to 50% and in yield increases of 10 to 25% within 10 days. The production and protein yields of peas were increased by 10% with PK sprays applied at flowering. Spraying with NPK or application late in the season was ineffective. Nagymihaly et al. (1959) also reported that spraying of peas with potassium or PK about the time of flowering tended to increase the dry matter percentage, and additional trace elements increased the fresh weight. Thorne (1954b) had pot experiments with barley, brussels sprouts, French beans, and tomatoes in soils at different nutrient levels. Plants were sprayed frequently with solutions containing NPK and calcium. The growth and nutrient content of the control plants, which were sprayed with water and spreader only, were practically identical with those of unsprayed plants. Lack of response of tomatoes was attributed to dilutions of spray solutions necessary to avoid damaging the leaves. The absorption of nitrogen, potassium, phosphorus, and calcium from mixed sprays did not correspond to the proportions in which the elements were mixed. Mel'nichuk (1960) reported that spraying with 2% NPK solution increased sweet pepper yields by 23%. Foliar nutrition of strawberries increased yields by 55 to 158%, and sprinkling seedlings of cherries and applies with 0.5% NPK solution significantly improved their growth.

Coffee: Ananth (1961) found that the phosphorus content in the leaves of coffee plants was significantly increased after phosphorus spraying, while Carne (1966) found in trials with mature *Coffea arabica* that a compound fertilizer containing 15% nitrogen, 15% P_2O_5 equivalent, and 15% K_2O equivalent plus a trace element mixture containing magnesium, manganese, copper, zinc, iron, boron, molybdenum, and sulfur gave the highest yield.

Cacao: Madero Bernal (1953) reported good results on the foliar fertilization of cacao with NPK nutrients mixed with pest control compounds. This way of fertilization was more economical than soil application. Phosphorus sources were glycerophosphate and orthophosphoric acid. Manjarras Castaneda (1953) also reported favorable results by spraying cacao either before or after pollination with a mixture of Ca- or K-glycerophosphates and orthophosphoric acid as a source of phosphorus, urea as a source of nitrogen, and KCl as a source of potassium.

Other crops: Sita Ram and Abraham (1970) found that the bundle strength of cotton was increased significantly when urea and orthophosphoric acid were sprayed in combination. Kiryakhin (1960) found that top dressing of potatoes at mass flowering increased the yield of tubers, starch, protein, and vitamin C on drained soils to which dung, NPK, Cu, B, and Mg had been applied before planting. The most effective top dressing was NPK, B, and Cu. Trzecki (1962), on the other hand, concluded that, with proper cultivation conditions of potatoes, a late supplementary fertilization by ordinary or foliar application gave no positive results. Polgar (1962) found that foliar sprays of NPK fertilizer produced increases in yield of rice similar to those obtained from soil application of quantities of fertilizer five to six times as great. Thomas (1960) increased the dry weight of maize with foliar application of monobasic potassium phosphate, calcium phosphate, or ammonium phosphate. Mokhtar (1968) did not find any increase of either flax seed or straw from two sprayings 45 and 50 days after sowing in comparison with the controls without any phosphorus or potassium addition. However, in this instance there was no yield response when the phosphorus and potassium were added to the soil. Williams (1958) found that spraying with NPK solutions gave smaller increases in yield than did less fertilizer applied to the soil and stated that spraying is likely to be economical for grassland only where top dressing is impossible, such as on marshes or inaccessible hill pastures where helicopters can be used. Mednis (1952) found that the most effective foliar application of NPK to clover was not more than 3 kg per hectare at the end of flowering. Homutescu et al. (1963) found that increases in yield of fodder beets due to applications of nitrogen, phosphorus, and potassium were 10 to 26%, 8 to 15%, and 5 to 7%, respectively. The best results with nitrogen were obtained when it was applied as root enlargement started. Phosphorus was best given in two doses, at the start of fruit enlargement and a month before harvest. Potassium had its best effect when given a month before harvest. The combined application of nitrogen, phosphorus, and potassium was more effective than application of only one of these elements, and the best time of application was the beginning of root enlargement rather than a month before harvest. Galgoczi (1967) found that the yield of fertilized sunflower grown on a poor sandy soil was increased 62% by one foliar application and 97% by two foliar applications of NPK solution. Corresponding increases in oil content were 1.61 and 2.78%.

G. Special Effects Resulting from Foliar Applications of Phosphorus

There are many quality factors, some real, others perhaps imagined, associated with foliar application of fertilizers. Color differences cannot always be translated into increased yields, but the improved appearance is justification enough for many growers to continue with the practice. Many difficult to define factors such as improvement in general appearance and improved luster, shipping quality, firmness, flavor, and color have been associated with foliar nutrition. Some quality improvement factors have been defined.

The sucrose content of sugar cane and regrowth of the ratoon crop have been significantly increased by preharvest sprays of phosphate (Carpenter, 1961).

Krzysch (1958a, 1958b) and Krzysch and Eberhardt (1960) reported an increase in resistance of oats to cereal mildew (Erysiphe graminis), and both nitrogen and phosphorus were effective in controlling this disease. The appearance of mildew in spring barley in pots was prevented by spraying with weak solutions (2 to 2.6%) of NPK, superphosphate, or potassium or ammonium nitrate. These nutrient sprays provided more effective control than did application of S or Cuprayit.

Il'inskij (1962) reported that the application of NPK in the autumn on fruit trees like apple, plum and sour cherry improved the frost resistance of the trees. Martem'yanov and Pshina (1973) reported that foliar application of superphosphate and potassium chloride solutions increased the growth and increased the winterhardiness of woody plants such as Tien Shan pearl bush, white mulberry, and silver fir, which are exotic under Moscow's climatic conditions.

Krivko (1966a) found that spraying of plums with phosphorus, potassium, and zinc increased the resistance of the plums to drought.

Naundorf (1954) found that a foliar application of a mixture of urea, calcium glycerophosphate, and potassium chloride to cacao reduced pod wilt and the percentage of withered beans, increased the yield of mature pods, increased the percentage of healthy beans, and gave a slight but nonsignificant reduction of pod rot.

Dorokhov (1957) reported an increase of the rate of photosynthesis by 30 to 60% as compared with control plants after application of an NPK mixture to the leaves of sugar beets. The maximum increase took place in the first day after treatment. The effect decreased slowly over a period of 7 to 11 days. A second spraying produced a similar effect which lasted longer than the first spray. Most effective was a 1.5% solution. Foliar sprays of phosphorus and potassium at the end of the vegetative period supported the initial level of photosynthesis. Uturgauri and Oniani (1963) found that a foliar application of phosphorus in combination with other elements, especially magnesium and manganese, increased the rate of photosynthesis in beet plants. Kovalik (1969) found that foliar application of growth substances plus NPK during bud formation and flowering of tomatoes raised the photosynthetic intensity, dry matter production, and content of sugar and vitamin C and reduced the acidity.

Kessler (1965) reported that citrus trees given Nutra-

Phos spray, a commercial spray product containing nitrogen and phosphorus, developed less leaf-drop following a hot dry wind in the autumn and that it was possible to reduce the amount of blossom shattering in grapes by spraying them with a solution containing zinc and phosphorus. A heavier fruit set occurred on many crops, annuals as well as trees. Zinc sprayed alone reduced sugar development, whereas a spray containing zinc and phosphorus tended to raise the sugar percentage. Kuretani (1972) found that defoliation of grapes was delayed when sprays containing phosphorus were applied before the rainy season started.

Mihajlova (1970) found that the root respiration and top growth of tomato plants were improved by spraying the plants grown in fumigated soil with superphosphate solutions at a concentration of 0.5% P_2O_5 equivalent.

Oliver (1952) suggested that the splash effect of surface-applied fertilizer may be valuable for increasing the phosphorus content of grasses.

Arora and Singh (1970) found that application of NPK sprays to guava, a tropical pear-shaped fruit, reduced fruit acidity by 7.5%, whereas reducing and nonreducing sugars and pectin content increased by 3.6, 2.4, and 6.9%, respectively.

Ocheretyanyi (1958) found that spraying of parental beets with superphosphate solution increased by 27 to 34% the productivity of industrial beets which were grown from seeds of the sprayed plants. The sugar content increased by 0.8 to 1.0% and the yield of sugar increased from 10 to 11.5 metric centner per hectare.

Kick and Hellwig (1959) found that the water consumption was greater where plant nutrients were applied to the foliage than to the roots.

H. Comparison of Efficiency of Foliar versus Soil Applications of Phosphorus

Wittwer et al. (1957) measured a much greater efficiency of foliar sprays than of soil treatment as a supplemental source of phosphorus for the development of tomato fruit. This was true with all the three criteria they used for evaluation, namely, (a) micrograms of phosphorus recovered in the fruit from the phosphorus applied, (b) the percentage of the total phosphorus in the fruit derived from that applied by the two methods, and (c) the percentage of the applied phosphorus recovered in the fruit. Mean values for micrograms of phosphorus and percentages of total phosphorus in the fruits derived from foliar treatments were more than double those for soil application even though approximately 10 times as much labile P was applied to the soil as adhered to foliage. The efficiency of utilization as measured by the percentage of applied phosphorus recovered in the fruit was approximately 20 times greater for the foliar applications than for the soil applications, the most pronounced differences being with crops grown on sandy soils. Somos et al. (1962) reported also that the foliar application of phosphorus to tomatoes was several times more efficient than soil application with respect to the phosphorus content of several plant parts. The sprayed plants were more resistant to mildew. Golikov (1958) found that, when a solution of labeled superphosphate was sprayed on tomato leaves, the uptake of P^{32} by young plants in the greenhouse did not exceed 10% of the amount applied and took place mainly during the first 2 days. A soil application of P^{32} was slowly assimilated until only 1% of the applied phosphorus was absorbed. Gapinski (1966) found that, when P^{32} was applied to the soil or was sprayed on the leaves of tomatoes at the first-flower stage, seven times more P^{32} was absorbed by the leaves than by the roots and that the rate of uptake by the leaves was also higher than the rate of uptake by the roots.

Hamdi et al. (1966) found that 5 kilograms of P_2O_5 equivalent sprayed per hectare on cotton gave an increase in yield three times as great as that obtained with 32 kg of P_2O_5 equivalent applied to the soil. Bodade (1965, 1966) found that an application of 50% of the nutrients to the foliage of cotton was equal in effectiveness to soil application of the full amount.

De and Singh (1963) found that foliar application of one-fifth to one-fourth of the quantity of nutrients required for soil application was as effective in increasing the yield of potatoes as was the application of the full dose to the soil. Mukherjee and Saxena (1966) reported that, when half of the fertilizer was applied as a foliar spray and half to the soil at planting, the result was an 18% increase in potato yields over those obtained with application of the full amount to the soil at planting. Half of the amount of fertilizer equally divided between soil and foliar application yielded as much as did the full amount applied to the soil. Soil application and foliar spray increased the phosphorus content in plants by 37% compared with the same amount of fertilizer applied to the soil.

Prasad and Brereton (1970) compared the effects of phosphate fertilizers applied to the leaves and the soil for potatoes and swedes. In terms of yield return per unit of phosphorus applied, foliar and soil applications were equally efficient. In the case of foliar applications, the absorbed phosphorus appeared to be partly retained in the leaves. Consequently, the high efficiency of uptake was not reflected in the dry matter response. Four sprays of orthophosphoric acid at the rate of 3.5 kg of phosphorus per hectare led to the accumulation in the plant of phosphorus in excess of the plant's ability to use it. The low efficiency of utilization of the absorbed phosphorus appeared to be the main factor limiting yield response. De Datta and Moomaw (1965) also reported that the extra absorbed phosphorus was not necessarily fully translocated or involved in metabolism.

Amer et al. (1966) found that five sprays of 1.2 to 1.8%

superphosphate solution which supplied 225 kg of superphosphate per hectare was 14 times more efficient than 1500 kg of superphosphate applied to the soil with respect to the percentage phosphorus in plants. In corn grain, the efficiency was about the same for both sources. Thorne claimed that, under field conditions, foliar sprays are usually two to three times more efficient than soil applications. Lecat and Sosa-Bourdouil (1952) came to the same conclusion.

Sato (1971) studied the foliar application of phosphorus to grapevines. Five to seven sprays of 0.2 to 0.4% of KH_2PO_4 were applied to individual grapevines grown in phosphorus-deficient soil which was fertilized with increasing amounts of phosphorus. Foliar sprays increased growth, hastened shoot ripening, increased yield, and improved fruit quality irrespective of the amount of phosphate fertilizer applied to the soil. It was found that the sprays increased the efficiency of the phosphate fertilizer applied to the soil. The sprays increased growth by producing a higher rate of carbon assimilation in the leaves; this caused increased root growth.

Kalmykova (1966) dipped the shoots of peach trees in a P^{32}-labeled solution of KH_2PO_4 and measured more rapid absorption and translocation during the intensive growth and flowering of the trees than was obtained with phosphorus applied to the soil. Most of the P^{32} remained in the treated shoot, its concentration decreasing with the distance from the place of application.

Meyer and Boodley (1964) found that only 0.75 to 1.5 g of H_3PO_4 per liter could be used safely as a weekly foliar application without pH adjustment. $NH_4H_2PO_4$ was safe to use at rates up to 1.7 g/l. They concluded that, regardless of materials and amounts used, weekly foliar applications were not as effective as additions of phosphorus to the soil for chrysanthemums or poinsettias.

I. Factors Affecting the Foliar Absorption of Phosphorus

There are many factors which affect the absorption of phosphorus by the leaves. Some of these factors are intrinsic to the plant, such as the age and physiological development of the leaf, leaf thickness, leaf surface, and varietal differences within the plant species. Other factors are environmental, like air humidity, temperature, phosphorus status of the growth medium, pH of the applied solution, and addition of sugars, surfactants, and growth substances. Tukey et al. (1956) and Wittwer et al. (1956) reviewed the various factors.

1. Leaf age and physiological development

The leaf is probably the most important variable in nutrient absorption. Wittwer and Lundahl (1951) established in 1951 the relatively greater nutrient absorption efficiency of young, expanding leaves than of full-grown, mature leaves of various vegetable crops. Koontz and Biddulph (1957) found that more phosphorus was translocated from older than from younger leaves in bean plants and that leaves contributed phosphorus to the root in proportion to their proximity to it. Ahlgren and Sudia (1964) found that absorption of P^{32} by both leaves and cotyledons of soybeans was greatest in immature leaves and decreased with increasing leaf age until a fairly steady state was reached. They found that immature trifoliate leaves do not export absorbed phosphorus, which suggests that it is utilized by the growing leaves and is not available for translocation. Transport of P^{32} also decreased with an increase of age, but to a smaller extent, which indicates that there is an increasing amount of P^{32} being transported and a decreasing amount retained by the treated leaves. Vogl (1960) found that young needles of spruce absorbed better than older ones; Fisher and Walker (1955) also measured higher rates of absorption in young than in old leaves of McIntosh apple. Ananth (1961) reported that the age of coffee leaves had no effect on the rate of phosphorus absorption.

Bukovac and Davidson (1961) reported that only 1% of the phosphorus applied to leaves of <u>Taxus cuspidata</u> was recovered in the roots after 12 days; 6% of the phosphorus recovered in the tops was derived from a single soil application of a water soluble fertilizer 12 days earlier although less than 0.5% of the applied fertilizer was absorbed. The limited absorption of foliar applications of P^{32} by <u>Taxus cuspidata</u> is of special interest. The extremely thick cuticular layer and specialized anatomical feature of the needle-like leaves of the yew may well largely prevent the entry of phosphorus.

Kaindl (1954) mentioned that the maximum uptake of labeled P through the leaves is associated with periods of maximum vitality.

2. Upper vs. lower leaf surface

The generally greater penetration of pesticides and nutrients through the lower leaf surfaces is often accredited to the thinner cuticle and greater number of somata found on that surface as compared to the upper, at least in most plant species. Burr et al. (1958) found that the lower leaf surface of sugar cane absorbs phosphorus more efficiently than the upper. Ursulenko (1958) noted that the uptake of P^{32} by the lower surface of apple leaves from a solution was more intense and lasted longer than the uptake by the upper surface of the leaves. Kaindl (1953, 1954) reported the greater entry of P^{32}-labeled KH_2PO_4 in the leaves of wheat and berries from sprays through the lower leaf surface than through the upper leaf surface, but the results were not directly comparable since the applied droplets covered a greater area on the lower surface. There is also one report of a greater absorption by the upper leaf surface than the lower leaf surface of tobacco plants (Takahashi and Yoshida, 1958).

3. Dependence on available energy

Srinivasan (1961) measured a maximum distribution of absorbed P^{32} within the seedlings of bean plants when they were exposed to unfiltered light. When seedlings were exposed to unfiltered light, the P^{32} was translocated to the underground portions of the seedlings in preference to the aerial portions; this did not occur in seedlings kept in darkness. Berzak (1962) also found that, in the dark, the amount of phosphorus absorbed by hemp leaves increased, the stem became the region of greatest accumulation, and root accumulation also increased. Ahlgren and Sudia (1967) concluded that phosphate uptake is an active process and is energy dependent. It is thus not surprising that light increases phosphate uptake. They claimed that the greater absorption by immature leaves is not due to fewer barriers, i.e., thinner cuticles, but is metabolically controlled and probably has an energy requirement.

4. <u>Moisture stress</u>

According to Van Overbeek and Bloudeau (1954), a favorable water balance is important for optimum foliar absorption and translocation. Swelling of the polar cutin with an ample moisture supply spreads the wax components farther apart and thereby enhances the permeability of the cuticle, particularly to water and water-soluble solutes. Pallas and Williams (1962) found that the absorption of P^{32} was influenced by moisture stress; more P^{32} was absorbed and about eight times as much was translocated below one-third atmosphere moisture tension as at approximately three atmospheres.

5. Influence of surfactants on foliar applications of phosphorus

The action of a surfactant may vary, depending on the nature of the penetrating solute and the type of surfactant. The number of reports of positive effects of surfactants is about equal to the number of reports of negative effects. Tween-20 was found to be ineffective in increasing the phosphorus penetration into bean leaves (Currier and Dybing, 1959); Triton X-100, however, improved phosphorus absorption. Fisher and Walker (1955) also found that Triton X-100 aided in the absorption of foliar applications of phosphorus. Taylor et al. (1962) tested nine surfactants, of which eight were found to reduce the adherence of the solution to bean leaves and markedly depressed phosphate absorption. Only one (Sterox AJ) increased the phosphorus absorption. Koontz and Biddulph (1957) tried eight surfactants. None increased and only two, Tergitol 7 and Vatsol OTB, decreased the percentage of phosphorus translocated in 24 hours from the leaves of the red kidney bean plant treated with 10 mM $NaH_2P^{32}O_4$ solution. Barrier and Loomis (1957) tried five surfactants, of which none significantly increased the absorption. Fisher and Walker (1955) measured a sevenfold increase in the apparent absorption of phosphorus with the addition of Triton X-100 to the KH_2PO_4 spray. Roldan et al. (1968) found at a 0.1% concentration of wetting agent that the decreasing order of phosphorus uptake was Tergitol, Sterox, Agricultural surfactant, Atlox 210, Triton X-400, Atlox 209, and glycerol. Cardoso et al. (1960) found that foliar absorption and translocation of P^{32} were doubled by adding the anionic wetting agent Fenopon AC-78 to the 0.1 molar monosodium phosphate spray. Cantliffe and Wilcox (1969) found that fat-sugar complexes used as surfactants raised ion uptake sometimes more than 20 times compared with no surfactant and, when compared with commercial surfactants, proved superior for use with foliar applications of phosphorus. Bester and Meynhardt (1968) found that the addition of surfactants such as Teepol, Carbowax, and Triton X-100 resulted in a significant decrease of phosphorus uptake. Teubner et al. (1957) reported also that surface active agents added to solutions reduced the adherence and depressed the phosphorus absorption. Eynard and Paglietta (1962) dipped olive and citrus leaves in a solution of P^{32} and one of six surfactants at 0.1% for 5 seconds and then counted the activity of the leaves with a Geiger-Müller counter. Statistically significant differences among surfactants were obtained. No correlation was found between the effect of the surfactant and the ionogenic class to which the surfactant belonged.

Boroughs and Labarca (1962) ascribed the enhanced foliar absorption associated with addition of a detergent to both a lowering of the contact angle on the exterior leaf surface and a facilitation of entry into the stomatal cavity. They measured an increased absorption of P^{32} by cotton plants when they used several surfactants in 0.1% concentrations. They found also that coffee plants translocated a constant percentage of their absorbed phosphorus independent of the surfactant used.

Glycerin is actually not a surfactant but rather a humectant. It prevents sprays from drying completely on the leaf surface. Koontz and Biddulph (1957) reported that glycerin increased the translocation of phosphorus. Fisher and Walker (1955) reported a sevenfold increase in phosphorus absorption when 2% glycerin was added to the spray solution. Takahashi and Yoshida (1958) also reported an increase in phosphorus absorption from addition of glycerin to the spray on tobacco. Bester and Meynhardt (1968), however, reported that glycerin did not affect the uptake of phosphorus by leaves.

6. Addition of sugars

The effect of sugars is about as controversial as that of surfactants. Yatazawa and Higashino (1952b) found that a 5% aqueous solution of glucose, fructose, and sucrose increased the phosphorus absorption by young wheat plants by threefold, suggesting that the movement of phosphorus from leaves is related to sugar in the leaves. Yatazawa and Tai (1953) found that glucose and fructose are most effective for increasing the transport of phosphate. The reason fermentable sugars are so effective in increasing phosphate transport is supposed to be the accelerative formation of phosphate esters in the mediation of energy-rich phosphate bonds in leaf cells in the presence of considerable amounts of inorganic phosphate. Much of the phosphate may be transported to other parts of the plant as sugar esters. Other authors like Ahlgren and Sudia (1967), Teubner et al. (1957), and Okuda and Yamada (1960) obtained no benefits from addition of sugars. Teubner et al. (1957) found that the addition of sucrose to solutions reduced the absorption but enhanced the transport of nutrients from leaves in plants which are low in sugar. Okuda and Yamada (1960, 1962) found that added sucrose had no effect on the absorption of phosphorus but that it might have an effect on the translocation.

7. Addition of other adjuvants

Borodulina and Ovcharov (1962) found that addition of nicotinic acid to the soil or to the leaves enhanced greatly the absorption of phosphorus by cotton plants from soil or leaves. The absorption of phosphorus from KH_2PO_4 was increased to a greater extent by nicotinic acid than was the absorption of phosphorus from superphosphate. Foliar application of nicotinic acid and superphosphate during the flowering period was reported to hasten boll maturation of cotton, to increase boll weight, seed weight, and yield of raw cotton, and to increase the content of phosphorus in the seed. Boroughs and Labarca (1961) found that the foliar absorption of P^{32} by seedlings of *Phaseolus vulgaris* was increased by application to the leaf surface of a few drops of pepsin, trypsin, and pectinase, but not by lipase, steapsin, papain, cellulase, or hemicullulase. Bukovac and Wittwer (1961) found that pretreatment of bean plants with specific growth substances altered foliar absorption and transport of some nutrients. Maleic hydrazide reduced the uptake of P^{32} and gibberellin and their subsequent transport to the roots. Kovalik (1969) found that 0.001% heteroauxin or 2,4-D added to NPK foliar sprays on tomatoes gave more yield increase than only NPK sprays.

8. pH of applied solution

Teubner et al. (1957) and Okudo et al. (1960) all found that maximum foliar uptake of phosphorus occurred with solutions at pH 2 to 3 when the carrier was the ammonium ion. Okudo et al. found another maximum at pH 5.6 to 6.2. Yeh (1967) also found that the rate of absorption of phosphorus was greater at pH 2 than at pH 3 or 4 regardless of the source of phosphorus. Chu and Ku (1966) found that, when the pH of the solution was 3, the proportion of the $P^{32}O_4$ remaining at the treated segment of rice leaves was lower than it was at any other pH value tested. The amount of retention increased with the pH values in the order of 2, 4, 5, and 6. Cardosa and Boroughs (1960) found that absorption and translocation were both affected by the pH, the highest values occurring between pH 5 and 6 and very low values at pH 7. Bester and Meynhardt (1968) found that leaves of grape vines absorbed phosphorus more readily from an orthophosphoric acid solution adjusted to pH 2.5 with potassium hydroxide than from a solution at pH 3.5 or pH 5.0. Phosphorus was absorbed from solution at pH 2.5 equally readily if the cation present was sodium or potassium. Phosphoric acid solutions of pH 1.5 caused severe leaf injury. When De Datta and Moomaw (1965) applied a potassium pyrophosphate solution to sugar cane at a pH of 11.25, it caused damage to the plants. They made subsequent sprayings at pH 5.3 after the solution had been adjusted with HNO_3, and no further damage was observed. Boroughs et al. (1963) found that the maximum absorption by cacao was at pH 2 with potassium phosphate, at pH 10 with ammonium phosphate, and at pH 5 with sodium phosphate. The translocation of sodium and ammonium phosphate was closely related to the absorption of these salts, but the translocation of potassium phosphate was almost independent of the pH. T'yuki et al. (1957) found that absorption from sodium phosphates was greatest at pH 6, and absorption from potassium phosphate was greatest at pH 7. Roldan et al. (1968) found that the optimum pH for uptake of phosphorus was 5 with NaH_2PO_4, 3 with KH_2PO_4, and 10 with $(NH_4)_2HPO_4$.

9. Effect of accompanying cation

Boroughs and Labarca (1962) found that absorption and translocation of phosphorus was greatest where the phosphate was accompanied by ammonium, less with sodium, and least with potassium. They measured 37% absorption of phosphorus from $NH_4H_2PO_4$ by coffee within 18 days. Teubner et al. (1957) also obtained the maximum absorption of phosphorus with ammonium as a carrier. Roldan et al. (1968) confirmed these findings. Bester and Meynhardt (1968) found no difference in absorption of phosphorus from solutions at pH 2.5 if the cation present was sodium or potassium.

10. The effect of phosphorus in the growth medium on the foliar absorption of phosphorus

There is considerable evidence that phosphorus in the growth medium is beneficial for the uptake of phosphorus applied to the leaves. Yatazawa and Higashino (1952a) found that the absorption of phosphorus from 0.1 molar KH_2PO_4 solution applied to the leaves was less with phosphorus-deficient plants than with plants on complete nutrient solutions, but that at 72 hours after application the rate of absorption was the same. Asen et al. (1954) found that foliar application of phosphorus to chrysanthemums had the greatest beneficial effect on growth when there was a low concentration of available phosphorus in the culture medium. Kaindl (1954) confirmed this for wheat and berries, and Ishihara (1958, 1960) stated that foliar sprays of phosphate on Japanese pear and apple seedlings produced the greatest increase in growth when combined with a soil application of phosphate. Singh and Pandey (1969) found that the increase in yield of Egyptian clover seed from a foliar application of phosphorus was more pronounced with a basal dressing of 2 quintals of superphosphate per hectare than without. Afridi and Samiullah (1973) found that the beneficial effect of phosphorus spray on the yield of barley was generally more pronounced when the plants had received a small dose of phosphatic fertilizer as a basal dressing (30 kg of P_2O_5 equivalent per hectare) than when they were grown without application of phosphorus to the soil. Silberstein and Wittwer (1951) noted that tomato plants grown with a foliar application of phosphorus produced 12% higher yields with a basal dressing of phosphorus to the soil than without. Thorne (1957) found that the uptake of phosphorus by the roots of swedes, but not sugar beet, grown with a high supply of phosphorus to the roots was decreased by applying sodium phosphate solution to the leaves. The top to root ratio for phosphorus content in milligrams per plant was greater for phosphorus absorbed via leaves than for phosphorus absorbed via roots. Increasing the phosphorus supply to the roots increased this ratio for phosphorus absorbed either via leaves or roots.

Barat and Das (1962) found that uptake of phosphorus by maize roots was enhanced by foliar application of phosphate as superphosphate.

There are also some reports about negative interactions due to the presence of phosphorus in the growth medium. Eggert and Kardos (1954) experimented with two-year-old apple trees receiving nutrient solutions with or without phosphorus in sand cultures. The trees were sprayed three to five times with solutions of $(NH_4)_2HPO_4$. The foliar absorption of phosphorus increased with increased numbers of sprayings, but was significantly depressed by the presence of phosphorus in the medium. They concluded from this that phosphorus sprays do not adequately provide all the requirements of trees other than those with a very low phosphorus supply to the roots.

11. The effect of temperature on foliar absorption

Teubner et al. (1957) found that the temperature optimum for utilization of phosphorus applied to bean leaves was about 21°C. Sekicka (1961) found that the optimum air temperature for P^{32} absorption was 30°C with sweet potatoes. Certain Russian researchers have been interested in studying the effect of temperature on the mineral nutrition of plants. Shtrausberg (1958) concluded that, at low soil temperatures, nutrition by foliar application seems to be more feasible than nutrition through the roots because uptake by leaves occurs more readily than by the roots. Zhurbitzky and Shtrausberg (1958) found that a decrease in soil temperature from 19°C to 6°C reduced the assimilation of root absorbed phosphorus by half, whereas the same reduction of air temperature produced almost no effect on assimilation of foliar applied phosphorus. Foliar application of phosphorus gave better results than doubling the dose of fertilizer applied to the soil at 7°C. Wittwer et al. (1956) found that under controlled conditions the uptake of foliar applied phosphorus increased directly with rise in temperature.

Phillips and Bukovac (1957) reported that the absorption of radiophosphorus by leaves of the bean and pea increased with an increase in the temperature of the root medium. P^{32} was exported from the treated leaf and accumulated to a greater extent in roots of plants grown at the higher (18 and 24°C) than lower (7 and 12°C) root temperatures. Bean leaves excised from plants grown for 1 to 4 days at root temperatures of 7, 13, 18, and 24°C continued to absorb P^{32} at rates which were a function of the temperature to which the roots were previously exposed. The greatest benefit from foliar sprays of phosphorus has been found when root temperatures and soil phosphate levels were inadequate for best growth (Asen et al., 1954; Higashino and Yatazawa, 1952). It has been suggested that foliar application of nutrients might extend the northern boundaries of successful crop production, where the limiting factor in growth may well be the inability of the plant root to extract sufficient nutrients from the cold soil (Klechkowski, 1956).

12. Energy dependence of foliar absorption

Teubner et al. (1957) found that the absorption by leaves is generally greatest during daylight. The overall process of foliar absorption is coupled with plant metabolism (Yung and Wittwer, 1963). Recent evidence indicates that foliar absorption of mineral nutrients is an active metabolic process. Mechanisms of ion uptake by leaves are similar to those for roots. Thus, foliar absorption is temperature, light, and oxygen dependent. This was confirmed by Srinivasan (1961) and Ahlgren and Sudia (1967). T'yuki et al. (1957) also found that absorption of phosphorus applied to leaves was greater in light than in darkness, and the difference disappeared in the presence of sucrose solution.

13. Effect of urea on the absorption of foliar applied phosphorus

Yamada et al. (1965) found that urea enhances not only its own absorption but also that of both cations and anions. Urea did not accelerate cellular absorption of phosphorus. It appears that urea significantly increases the uptake of many nutrient ions into leaves. With cations, this apparently occurs at both the cuticular and cellular levels. It was independently confirmed by Mukherjee et al. (1966) and Okuda and Yamada (1962) that the effectiveness of phosphorus sprays was greatly enhanced if urea was added to the spray solution. However, Tormann et al. (1969) and Chu and Ku (1966) found that the addition of urea to phosphoric acid sprays on applies had no effect on the uptake.

Grechushnikov and Kiryukhin (1962) found in pot experiments with sodium phosphate sprays on potatoes that the use of urea did not increase the movement of P^{32} into the tubers.

14. Effect of solution concentration on phosphorus absorption

It was found by Eggert and Kardos (1954), Koontz and Biddulph (1957), and Berzak (1962) that the foliar absorption of phosphorus increased with the number of sprayings, the amount of phosphorus applied, and the concentration in the solution. It should be realized, of course, that the chance for damage to the leaves also increases as the amount of phosphorus applied becomes greater.

15. Air humidity and time of application

Kaindl (1953), Koontz and Biddulph (1957), and Rid (1964) all found that spraying in the evening is the best because of slowest drying. Dew formation in the morning remoistens the residue of nonabsorbed salt.

III. REVIEW OF UNPUBLISHED WORK

A. Introduction

It was noted in the literature review that orthophosphoric acid is one of the best compounds that has been tested for foliar application of phosphorus. The practical value of such applications of orthophosphoric acid, however, is limited by the fact that concentrations higher than 0.5% phosphorus cause considerable damage to the leaves. The quantity of phosphorus that can be applied to a crop in the juvenile stage, when the relative requirement for phosphorus is greatest, is only 1 to 2 kg per ha. Far greater quantities of nitrogen can be safely applied in the form of urea, as was observed in the literature review.

Dr. P. K. Hanley, a former graduate student of Dr. C. A. Black, started to investigate the hypothesis that nonionic phosphorus compounds might be less toxic than ionic compounds. This hypothesis was based on the superior performance of urea as a source of nitrogen. Hanley investigated also the influence of adding urea and/or sucrose to the solution of the phosphorus compounds. John Phillip, another former graduate student of Dr. C. A. Black, investigated the influence of neutralization of phosphoric acid and addition of glycols on the damage done to the leaves and on the absorption of the phosphorus applied. The information contained in this portion of the thesis was extracted from the notebooks of the two students mentioned. It represents the preliminary work on which the research in this thesis was based.

B. Foliar Application of Several Organic Phosphates to Soybeans

Volumes of 0, 12.5, and 50 microliters of solutions of seven organic phosphates and one inorganic phosphate containing 0, 9.7, and 38.7 μg of P were applied by means of a micrometer syringe to selected portions of soybean leaves on January 3, 1966. The treated area was 1 cm in diameter and was marked by dipping a cork borer in warmed lanolin and making a circle on the leaf. All the solutions contained 0.05% Tween-80 to lower the surface tension.

Seven days after application of the phosphorus compounds, the treated portions of the leaves receiving the 50-μl applications were cut out and shaken in a detergent solution to remove the phosphorus that had not been absorbed. The washings were digested with nitric and perchloric acids, and the phosphorus was determined by the method of Dickman and Bray, as modified by Legg and Black (1955). To serve as controls, washings derived from the untreated leaf areas as well as 50-μl aliquots of the original phosphate solutions were carried through the phosphorus determination. Phosphorus not found in the leaf washings was assumed to have been absorbed.

The results of this experiment are summarized in Table 1.

Table 1. Absorption of phosphorus from monobasic potassium phosphate and various organic phosphates by soybean leaves, and damage to the leaves associated with the various applications seven days after application

Phosphorus compound	P applied ($\mu g/cm^2$)	pH of solution	P absorbed, % of added P	Leaf damage
Dimethyl phosphate	81.7	1.8	95	Slight
Trimethyl phosphate	49.5	2.9	96	None
Diethyl phosphate	51.0	1.7	74	None
Triethyl phosphate	19.6	3.7	14	None
Tripropyl phosphate	12.1	3.7	100	Severe
Dibutyl phosphate	60.1	1.8	68	Slight
Tributyl phosphate	10.0	5.1	100	Severe
Potassium phosphate (monobasic)	49.5	5.1	91	None
Control	0	4.2	-	None

The results indicate that the usefulness of these phosphorus compounds, based on phosphorus absorption and leaf damage, followed the sequence of KH_2PO_4, trimethyl phosphate > dimethyl phosphate > diethyl phosphate > dibutyl phosphate > triethyl phosphate > tributyl phosphate > tripropyl phosphate. In general, diphosphates were better than triphosphates, and the order of usefulness of the phosphate esters of the various alcohols was methyl > ethyl > butyl > propyl. The pH of the solutions of the organic phosphates ranged from 1.7 to 5.1, which may provide some explanation for the damage they did to the leaves.

C. Effects of Urea and Sucrose

Urea has found considerable use as a spray to supply nitrogen to plants. Urea is readily absorbed from foliar applications. Urea is a weak base and forms with phosphoric acid the compound urea phosphate, $CO(NH_2)_2 \cdot H_3PO_4$, which crystallizes from a concentrated solution. The acidity of urea phosphate is almost as great as that of the phosphoric acid in the absence of the urea.

The foregoing hints with respect to the action of urea suggest the possibility that the bonding of urea and phosphoric acid might aid in penetration of the phosphoric acid into leaves. Moreover, the action of urease inside plant cells should hydrolyze the urea to ammonium, which would neutralize the phosphoric acid and decrease the possible disturbance of metabolism as a result of uptake of phosphoric acid.

In the FAO publication, "Efficient use of fertilizers", the statement is made that 3 kg of urea per 500 liters of water has been found safe as a spray for tomato but that 30 kg of urea in 500 liters of water was still safe when the solution also contained 183 kg of cane sugar per 500 liters. The reason for the beneficial effect of sucrose was not stated and probably is unknown; however, it seems reasonable that the sucrose forms a syrup as the water evaporates and prevents the urea from attaining a toxic concentration.

There may also be chemical interaction between urea and sucrose. Ellerton and Dunlop (1966) reported the formation of urea-urea and urea-sucrose dimers in solution, which should reduce the toxicity due to the effect of solutes in increasing the solute suction of the aqueous solution placed on the leaves. Calculations of the possible loss of numbers of solute molecules due to the associations mentioned, however, indicate that the magnitude of these effects is not great enough to account for either the low toxicity of urea alone or the reduction in toxicity of urea when it is mixed with sucrose, and of course these effects could not account for the low toxicity of sucrose alone. Some other explanation must be sought. Two possibilities are that (a) both sucrose and urea produce approximately neutral solutions and (b) neither sucrose nor urea is ionic. Sucrose might be helpful in reducing damage from phosphoric acid as well as from urea.

A factorial experiment was done with three levels of phosphoric acid, 0, 31.0, and 92.9 µg of P; four levels of urea, 0, 60.1, 180.2, and 540.5 µg; and three levels of sucrose, 0, 342.3, and 3080.7 µg in 25 µl of solution applied to a leaf area of 1.13 cm^2. All solutions contained 0.1% Tween-80.

On may 25, 1966, when the second set of trifoliate leaves was well developed, the treatments were applied to separate leaflets of soybean plants grown individually in soil in plastic containers in the greenhouse. The three replications were arranged at random in blocks.

Estimates of leaf damage were made 11 days after application of the treatments. Fourteen days after application of the treatments, the treated areas were punched out with a No. 7 corkborer. The leaf discs were immersed for 10 minutes in 10 ml of 0.1% Tween-80 solution, after which the leaf washings were analyzed for total phosphorus. The results are presented in Table 2.

Inclusion of sucrose in the solution applied to soybean leaves much reduced the damage rating and the damaged area resulting from application urea and, to a lesser extent, phosphorus. No damage was noted from sucrose alone. Sucrose had no apparent effect on the phosphorus absorption. The extent of the leaf damage resulting from application of both orthophosphoric acid and urea exceeded the sum of the damage caused by the treatments individually. In terms of leaf damage, this is a positive interaction between urea and phosphoric acid. Urea did not seem to influence phosphorus absorption, but this is, of course, hard to judge with nearly all values for absorption exceeding 90%.

The effect of sucrose and urea on the absorption might have been different in an experiment of shorter duration. The rate of absorption, however, was not of so much concern as the leaf damage caused by the phosphoric acid.

The original concentration of the highest phosphoric acid

Table 2. Absorption of phosphorus by soybean leaves from phosphoric acid applied to the leaves with various additions of urea and sucrose, and damage to the leaves associated with the individual treatments

Treatment			Damage estimation		P absorbed as % of P applied
H_3PO_4 (μg P/cm^2)	Urea (μg/cm^2)	Sucrose (μg/cm^2)	Damage rating[a]	Damaged area[b]	
0	0	0	0	0	-
0	0	908.8	0	0	-
0	0	2726.3	0	0	-
0	53.1	0	0	0	-
0	53.1	908.8	0	0	-
0	53.1	2726.3	0	0	-
0	159.4	0	1	0	-
0	159.4	908.8	0	0	-
0	159.4	2726.3	0	0	-
0	478.3	0	3	25	-
0	478.3	908.8	3	15	-
0	478.3	2726.3	1	3	-
27.4	0	0	2	14	96
27.4	0	908.8	2	15	99
27.4	0	2726.3	2	12	96
27.4	53.1	0	2	16	96
27.4	53.1	908.8	2	20	97
27.4	53.1	2726.3	2	13	95
27.4	159.4	0	3	20	97
27.4	159.4	908.9	2	16	98
27.4	159.4	2726.3	2	13	98
27.4	478.3	0	3	50	97
27.4	478.3	908.9	3	42	98
27.4	478.3	2726.3	2	17	98
82.2	0	0	3	37	94
82.2	0	908.8	3	35	88
82.2	0	2726.3	2	35	98

[a]Code for damage ratings: 0 = none apparent; 1 = damaged area dark in color but apparently not dead; 2 = damaged area mostly dark in color and apparently dead, sometimes with small areas light tan to gray in color and obviously dead; 3 = damaged area mostly or entirely light tan to gray in color and obviously dead.

[b]Damaged area is the sum of the damage inside and outside the treated area in % of the treated area.

Table 2. (Continued)

Treatment			Damage estimation		absorbed
H_3PO_4 (μg P/cm^2)	Urea (μg/cm^2)	Sucrose (μg/cm^2)	Damage rating	Damaged area	as % of P applied
82.2	53.1	0	3	54	96
82.2	53.1	908.8	3	51	92
82.2	53.1	2726.3	2	26	80
82.2	159.4	0	3	67	96
82.2	159.4	908.8	3	42	94
82.2	159.4	2726.3	2	33	77
82.2	478.3	0	3	57	98
82.2	478.3	908.8	3	51	99
82.2	478.3	2726.3	2	31	96

application was 0.12 mole per liter, and the concentration would increase with evaporation of the water. Such a solution might damage leaves on account of acidity, concentration, or both. One may note, however, that the solute suction of the strongest solution of urea and sucrose together much exceeded that of the phosphoric acid but still produced only minor damage. Hence, the acidity of the phosphoric acid may be the major factor responsible for the leaf damage. To judge from Hanley's analyses of leaf washings, the absorption of the phosphoric acid was good. The main problem seems to be to obtain absorption without damage.

D. Effect of Neutralization and Addition of Glycols on Phosphorus Absorption

It is not certain that the leaf damage due to addition of phosphoric acid was a consequence of acidity, but it was thought to be worth trying some substances that would reduce the acidity at the same time as they might have properties that would promote absorption. Organic substances might be expected to have more solubility in cutin than would inorganic substances that could be used to neutralize the phosphoric acid. Although the significance of the nitrogen content of urea in affecting the uptake of this substance is not known, the facility with which urea is absorbed and the large quantities taken up suggest the possibility that certain simple organic substances containing nitrogen might facilitate uptake of phosphorus if at the same time they reduce the acidity. The properties of several organic substances that seemed of interest in this connection are shown in Table 3.

Monoethanolamine, $HOCH_2CH_2NH_2$, is a moderately viscous liquid. As a base, it has about the same strength as ammonia. It is very hygroscopic, and it forms soaps with free fatty acids.

Diethanolamine, $(HOCH_2CH_2)_2NH$, is a crystalline, white solid with a melting point of 28°C. Its most important property is the ability to combine directly with acids.

Triethanolamine, $(HOCH_2CH_2)_3N$, is a viscous and very hygroscopic liquid. Its alkalinity is less than that of

Table 3. Certain properties of monoethanolamine, diethanolamine, and triethanolamine[a]

Compound	Mol. weight	Boiling point (°C)	Vapor pressure (mm Hg at 20°C)	pH in 25% sol.	Solubility (% w/w at 25°C)
Monoethanolamine	61.08	170.5	0.4	12.1	Complete
Diethanolamine	105.14	269.1	<0.01	11.5	95.4
Triethanolamine	149.19	360.0	<0.01	11.2	Complete

[a]Organic nitrogen compounds, 1946, Carbide and Carbon Chemicals Corporation, New York, N.Y.

ammonia. It forms soaps with free fatty acids. It is very effective in emulsifying oil, fat, or wax. It is used to emulsify insecticide spray oils. Because of their limited alkalinity, such sprays cause considerably less foliage damage than do those made with caustic alkalies. A small percentage of triethanolamine assists in the penetration of liquids into porous materials.

Other simple organic nitrogen compounds with basic properties that might be valuable include the following: ethylamine, $CH_3CH_2NH_2$; diethylamine, $CH_3CH_2NHCH_2CH_3$; and triethylamine, $(CH_3CH_2)_3N$.

Sucrose was relatively ineffective in preventing damage from phosphoric acid in Hanley's work, but this does not mean that other substances would be similarly ineffective. Gray (1956) reported that glycerol increased the absorption of streptomycin applied to leaves and flowers. The 1% solution used in his work corresponds to a concentration of 2.74 micromoles per 25 microliters of solution. In Hanley's work, the highest concentration of sucrose used was equivalent to 9 micromoles per 25 microliters of solution.

Glycerol has the formula $CH_2OH{\cdot}CHOH{\cdot}CH_2OH$. The molecular weight is 92.06. Glycerol is only one of a number of compounds with similar structure. Others include (a) ethylene glycol, $HOCH_2CH_2OH$, with a molecular weight of 62.07; (b) diethylene glycol, $HOCH_2CH_2\text{-}O\text{-}CH_2CH_2OH$, with a molecular weight of 106.12; and (c) triethylene glycol, $HOCH_2CH_2\text{-}O\text{-}CH_2CH_2\text{-}O\text{-}CH_2CH_2OH$, with a molecular weight of 150.17.

Phillip conducted an experiment in which 0, 1, and 3 micromoles of phosphoric acid were applied in a total volume of 25 microliters to a circular area of soybean leaf surface with a diameter of 1.2 cm. The circular area was delineated with a vaseline ring. The phosphoric acid was applied in water or in water containing 9 micromoles of glycerol, ethylene glycol, diethylene glycol, or triethylene glycol. The phosphoric acid was either unneutralized or neutralized to pH 7.0 with ethylamine, diethylamine, triethylamine, ethanolamine, triethanolamine, or ammonium hydroxide. All solutions contained 0.1% Tween-80. The experimental design was a completely randomized design with four replications. The treatments were applied on November 2, 1968.

Estimates of leaf damage were made on the 6th day after the solutions were applied and again on the 18th day. The means of the estimates for damage rating and damaged area will be found in Table 4. The results of the second series of observations show more damage than the first group and suggest a certain amount of hidden damage was present when the first observations were made.

Glycerol, ethylene glycol, and diethylene glycol caused some damage when applied alone. Triethylene glycol caused considerable damage when applied without phosphorus. Where the phosphoric acid was neutralized with ethylamine, diethylamine, or triethylamine, the leaf damage was generally greater than

Table 4. Damage to leaves of soybeans resulting from various applications of phosphoric acid, amines, glycols, and glycerol in Phillip's first experiment

Base used to neutralize the H_3PO_4 to pH 7	H_3PO_4 µg P per cm^2 of leaf surface	Damage to leaves observed			
		None		Ethylene glycol, 8 µmol	
		6 days	18 days	6 days	18 days
None	0	0[a] 0	0 1	0 0	0 1
	27.4	15 3	15 1	5 3	8 1
	82.2	27 3	42 1,2	20 2,3	22 1
Ethylamine	27.4	9 1,$\underline{3}$	19 1	12 3	18 1
	82.2	30 2	150 2,$\underline{3}$	16 2,3	231 2,$\underline{5}$
Diethylamine	27.4	1 3	182 3,$\underline{4}$	24 2,3	71 $\underline{2}$,3
	82.2	36 2,3	261 2,3	64 2,3	317 4,5

[a]The upper lines give the damaged area as the sum of the damage inside and outside the treated area in percent of the treated area. The second lines give the damage rating according to the following codes: Code for damage rating of 6th day: 0 = no apparent damage; 1 = damaged area discolored, but apparently not dead; 2 = damaged area mostly dark in color with small dead spots; 3 = damaged area mostly or entirely light tan to gray and obviously dead. Code for damage rating of 18th day: 1 = normal, except for possible small spots; 2 = one-third or less of leaf area showing some yellowing; 3 = one-third to two-thirds of leaf area yellowed; 4 = two-thirds to all of leaf area yellowed; 5 = entire leaf dead. Two numbers for the damage rating mean about equal area of both; underlining one of them indicates about two-thirds of the total damaged area has that rating.

at indicated times after specified additions of glycols or glycerol per 1 cm^2 of leaf surface

Diethylene glycol, 8 µmol		Triethylene glycol, 8 µmol		Glycerol, 8 µmol	
6 days	18 days	6 days	18 days	6 days	18 days
18 3	22 1	25 3	56 2	1 3	2 1
11 3	19 1,2	22 3	34 1,2	16 3	15 1
11 2	25 1,2	49 3	100 2	21 1,3	45 1
6 3	8 1	25 2	62 1,2	7 2	17 1,2
27 3	136 1,5	52 3	102 2	44 2	292 2,5
14 3	32 2	27 3	52 2	9 2	95 2,3
47 2,3	132 2,4	28 3	95 2	47 1,2	231 4,5

Table 4. (Continued)

Base used to neutralize the H_3PO_4 to pH 7	H_3PO_4 µg P per cm^2 of leaf surface	Damage to leaves observed			
		None		Ethylene glycol, 8 µmol	
		6 days	18 days	6 days	18 days
Triethylamine	27.4	15 2	34 1,2	2 1,2	22 1,3
	82.2	23 2	121 2	23 2,3	210 3,5
Ethanolamine	27.4	8 2,3	7 1	0 0	2 1
	82.2	6 1,2	21 1,2	11 2,3	34 2
Triethanolamine	27.4	2 1,2	4 1	6 2	8 1
	82.2	3 1,3	5 1	2 1	19 1,2
Ammonium hydroxide	27.4	0 0	0 1	1 2	5 1
	82.2	4 2,3	8 1	8 2	10 1

at indicated times after specified additions of glycols or glycerol per 1 cm^2 of leaf surface

Diethylene glycol, 8 μmol		Triethylene glycol, 8 μmol		Glycerol, 8 μmol	
6 days	18 days	6 days	18 days	6 days	18 days
15 3	21 1,2	17 3	44 2,3	11 1,3	31 1,2
11 2	51 1,2	26 1,3	74 2	19 2	59 2
12 3	14 1	32 3	35 2	5 3	7 1,2
27 3	62 2	34 3	81 2	7 3	39 1,2
21 3	25 1	39 3	71 1,2	3 2,3	8 1
7 3	27 2	32 3	41 1,2	17 1,3	33 1,2
9 3	27 2	26 3	40 1,2	7 1,3	11 1
22 3	29 1	25 3	29 2	26 2,3	27 1,2

it was where no neutralization was practiced, and was in no instance lower with both phosphoric acid additions. Where the phosphoric acid was neutralized with ethanolamine, leaf damage was consistently lower than without neutralization in the presence of glycerol and in the absence of glycerol and the glycols; however, the damage was still substantial. With both triethanolamine and ammonium hydroxide as neutralizing agents, the damage was relatively low in the absence of glycerol or the glycols. On the average, the leaf damage was slightly less with ammonium hydroxide than with triethanolamine as neutralizing agent.

On the basis of the results in the experiment just described, another experiment was conducted using more recently developed leaves on some of the same soybean plants. The purpose was to recheck the results obtained with what seemed to be the best treatments in the preceding experiments. In the follow-up experiment, with eight replications, the estimates of damage to the leaves were made on the 7th day following application of the treatments. The means are given in Table 5.

The amount of damage to the leaves was similar in the presence and absence of ethylene glycol. Damage from phosphoric acid was greatest where the phosphoric acid was not neutralized, less where it was neutralized with ethanolamine, still less with triethanolamine, and least where it was neutralized with ammonium hydroxide. Neutralization with ammonium

Table 5. Damage to leaves of soybeans resulting from various applications of phosphoric acid, amines, and ethylene glycol in Phillip's second experiment

Base used to neutralize the H_3PO_4 to pH 7	H_3PO_4 (μg P/cm^2)	Damage to leaves with: No ethylene glycol — Damage rating[a]	No ethylene glycol — Damaged area[b]	Ethylene glycol, 8 $\mu mol/cm^2$ — Damage rating	Ethylene glycol, 8 $\mu mol/cm^2$ — Damaged area
None	0	0	0	0	0
	27.4	2	17	2	9
	82.2	2	40	2	48
Ethanolamine	27.4	2	9	2	7
	82.2	2	26	2	18
Triethanolamine	27.4	1	7	1	2
	82.2	1	8	1	17
NH_4OH	27.4	0	0[c]	2	4[c]
	82.2	0	0[c]	1,2	1[c]

[a]Code for damage rating: 0 = normal; 1 = discolored but apparently not dead; 2 = dead.

[b]The damaged area is given as the sum of the dmaaged area inside and outside the treated area as a percentage of the treated area.

[c]White residue on treated area.

hydroxide was the best way to avoid the damage to the leaves. It should be mentioned here, however, that in the treatments involving the heavier application of ammonium phosphate (3 micromoles of phosphorus per 25 microliters), the treated area was covered by a white residue in the absence of glycerol or the glycols. Consequently, it is possible that much of the phosphorus added was still present on the surface. No analyses of leaf washings were done in this experiment. Consequently, it is possible that, from the standpoint of the effectiveness of the applied phosphorus in promoting plant growth, the ammonium phosphate treatment might be inferior to some of the others.

E. Absorption of Foliar Applications of Phosphoric Acid by Corn and Soybeans

Because Phillip's first two experiments did not give any information on the absorption of phosphorus from different treatments, a third experiment was conducted. The third experiment was similar to the second except that the treatments were applied to both corn and soybeans and that provision was made for determining the absorption of the phosphorus.

Plastic pots containing 945 grams of soil were planted on May 31, 1969, with soybeans, variety Hawkeye, and with a single-cross variety of corn. On July 29 and 30, quantities of 0, 1, or 3 micromoles of phosphoric acid were applied in a total volume of 25 microliters to a circular area of leaf surface with a diameter of 1.2 cm. The rings were made by means of a cork borer dipped in warmed lanolin. The phosphoric acid was applied in water or in water containing 9 micromoles of ethylene glycol, and the acid was either unneutralized or neutralized to pH 7.0 with ethanolamine, triethanolamine, or ammonium hydroxide. All solutions contained 0.1% Tween-80. The experiment was arranged as a completely randomized block design with eight replications.

Leaf damage estimates were made 2 days after the solutions were applied. On the 3rd day, half of the replications were sampled by punching out the treated area with a No. 7 cork borer. The leaf discs were transferred to a 2-ounce bottle containing 10 ml of a 0.1% detergent solution and were shaken for 5 minutes to dissolve the unabsorbed phosphorus. Estimates of the leaf damage on the remaining four replications were made 19 days after the treatments were applied. Leaf washings were prepared from leaf discs collected on the 20th day. Most of the corn leaves were dead before the second sampling, and for this reason only a few observations of damage were available. No leaf samples of corn were taken at the time of the second sampling. All leaf washings were analyzed for total phosphorus by the method of Dickman and Bray (1940) as modified by Legg and Black (1955).

The results for soybeans are given in Table 6. The addition of ethylene glycol caused a tremendous increase in damage during the 17 days between the first observation and the second, which is a good enough reason to consider only the long-term data. There was no instance in which the addition of ethylene glycol did not cause an increase in damage to the leaves. Neither the damage resulting from application of phosphoric acid nor the absorption of the phosphorus were markedly influenced by neutralization of the phosphoric acid with ethanolamine or triethanolamine. Neutralization of the

Table 6. Damage to leaves of soybeans resulting from applications of phosphoric acid, amines, and ethylene glycol in Phillip's third experiment, and absorption of applied phosphorus by the leaves

Base used to neutralize the H_3PO_4 to pH 7	H_3PO_4 µg P per cm^2	Leaf damage in 2 days		P absorbed in 3 days as % of P applied
		Rating[a]	Area[b]	
		No ethylene glycol addition		
None	0	0	0	-
	27.4	2	21	87
	82.2	2	69	87
Ethanolamine	27.4	1	6	74
	82.2	1,2	51	83
Triethanolamine	27.4	1,2	15	78
	82.2	1,2	59	79
Ammonium hydroxide	27.4	2	5	84
	82.2	2	16	84
		With addition of ethylene glycol, 245.7 µg/cm^2		
None	0	$1,\underline{2}$	56	-
	27.4	2	100	86
	82.2	2	97	85
Ethanolamine	27.4	$1,\underline{2}$	16	86
	82.2	$1,\underline{2}$	17	92
Triethanolamine	27.4	1,2	11	85
	82.2	$1,\underline{2}$	34	91
Ammonium hydroxide	27.4	$1,\underline{2}$	41	85
	82.2	$1,\underline{2}$	29	89
No. of replications		8	8	4

[a]Code for damage rating: 0 = normal; 1 = discolored but not yet dead; 2 = dead. Two numbers for the damage rating signify about equal areas of both degrees of damage. Underlining one number indicates that about 2/3 of the total damaged area has that rating.

[b]The damaged area is the sum of the estimated damaged area inside and outside the treated area in % of treated area.

Leaf damage in 19 days		P absorbed in 20 days as % of	Increase in 17 days from 1st to 2nd sampling (% of 1st application)	
Rating	Area	P applied	Damage	P absorbed
0	0	-	0	-
1,2	19	93	-10	7
2	54	93	-22	7
1	6	76	0	3
1,2	56	92	10	11
2	25	93	67	19
1,2	75	92	27	16
1	3	85	-40	1
1,2	11	92	-31	10
2	90	-	61	-
2	100	78	0	-9
2	112	88	15	4
1,2	20	80	25	-7
1,2	66	90	288	-2
1,2	55	89	400	5
1,2	62	91	82	0
1,2	76	86	85	1
2	96	84	231	-6
4	4	4	4	4

phosphoric acid with ammonium hydroxide produced the least damage, and the absorption of the phosphorus appeared to be good.

The results for corn are given in Table 7. From the very few observations available 19 days after application of the solutions, it appears that there was little increase in damage to the leaves between the 2nd day and the 19th day. Because observations on the 19th day were so incomplete, due to death of the leaves, the comparisons in Table 7 are confined to observations made on the 2nd day after application of the solutions. Ethylene glycol alone resulted in some damage to the leaves. In contrast to the behavior observed with soybeans, however, putting phosphoric acid and ethylene glycol together decreased the damage to the leaves. Ethanolamine as a neutralizing agent produced less leaf damage than did triethanolamine. Again, ammonium hydroxide as a neutralizing agent produced the least damage. There was less absorption of phosphorus from ammonium phosphate than from any other treatment, but the uptake of 86 and 78% of the phosphorus within 3 days after application is still good. Phillip mentioned in his notes that there was no visible residue on leaves treated with ammonium phosphate in this experiment.

Table 7. Damage to leaves of corn resulting from applications of phosphoric acid, amines, and ethylene glycol in Phillip's third experiment, and absorption of applied phosphorus by the leaves

Base used to neutralize the H_3PO_4 to pH 7	H_3PO_4 added µg of P per cm^2 of leaf surface	Leaf damage in 2 days		P absorbed in 3 days as % of P applied
		Rating[a]	Area[a]	
	No ethylene glycol addition			
None	0	0	0	-
	27.4	2	8	94
	82.2	2	44	97
Ethanolamine	27.4	1	8	85
	82.2	1	9	92
Triethanolamine	27.4	1,2	8	90
	82.2	1,2	41	88
Ammonium hydroxide	27.4	0	0	86
	82.2	0	0	78
	With addition of ethylene glycol, 246.7 µg/cm^2			
None	0	1,2	7	-
	27.4	1,$\underline{2}$	12	96
	82.2	$\underline{2}$	31	96
Ethanolamine	27.4	1,2	6	91
	82.2	1	1	94
Triethanolamine	27.4	1	11	93
	82.2	1	8	96
Ammonium hydroxide	27.4	1,$\underline{2}$	5	93
	82.2	$\underline{2}$	7	96
No. of replications		8	8	4

[a]See footnotes to Table 6.

IV. SCREENING OF PHOSPHORUS COMPOUNDS

A. Materials and Methods

1. Introduction

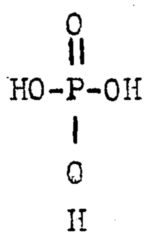
It appeared from the literature and previous work in this laboratory that none of the phosphorus compounds tested heretofore could be applied in high enough concentrations to the leaves to contribute significantly to the phosphorus requirement of corn and soybeans without damaging the leaves. It was therefore considered important to screen additional phosphorus compounds. The preliminary work indicated that, among the compounds tested, the principal problem was the toxicity of the applied phosphorus rather than the absorption. Several possibilities for reducing the toxicity seemed to exist.

One way that was considered as a possibility for reducing the toxicity was to neutralize orthophosphoric acid with an appropriate organic base, to associate the phosphate with organic nitrogen, or both. Examples of organic substances that came to mind as possibilities in this connection were choline, guanidine, and guanylurea.

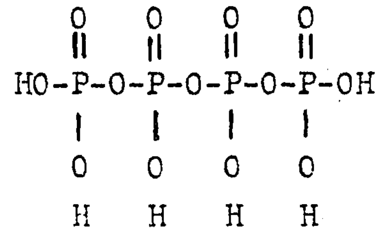
A second way of reducing the toxicity might be by lowering the solute suction per unit of phosphorus in the applied solution. Condensed inorganic phosphates as a group have this property. These substances are chain or ring compounds in which phosphate groups are joined with elimination of one molecule of water for each phosphate group added. The simplest ones are chain compounds like pyrophosphoric acid, tripolyphosphoric acid, and tetrapolyphosphoric acid, having two, three, and four phosphate groups, respectively. Their structural formula is given in Figure 1. Trimetaphosphoric acid and tetrametaphosphoric acid have, respectively, three and four phosphate groups in a ring structure. Others that contain mixtures of higher molecular weight phosphates, up to 10^4 to 10^6, are potassium metaphosphate and calcium metaphosphate.

The phosphorus-oxygen-phosphorus bonds in condensed phosphates are unstable. The compounds slowly hydrolyze in water. Plants contain enzymes that will split these bonds, making the individual phosphate groups available for metabolic purposes (Van Wazer, 1958, pp. 435, 490-499). Cells of at least some plants contain condensed phosphates. Therefore, condensed phosphates would not be expected to have toxic effects due to chemical configurations that are foreign to plants.

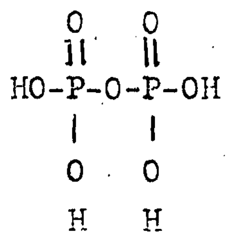
Condensed phosphates might be expected to have less toxic effect than equivalent amounts of orthophosphate for several reasons. First, the condensation reduces the molar concentration of the solution. Second, the number of ionizable hydrogens per phosphate group is less than in orthophosphate; this is especially true for calcium phosphates. Brown and Lehr (1964) observed that treatment of high-molecular-weight calcium metaphosphate with ammonium fluoride yields no precipitate of



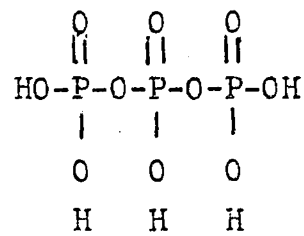
ORTHOPHOSPHORIC
ACID



TETRAPOLYPHOSPHORIC
ACID

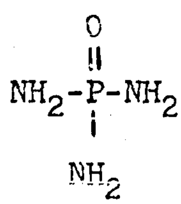


PYROPHOSPHORIC
ACID

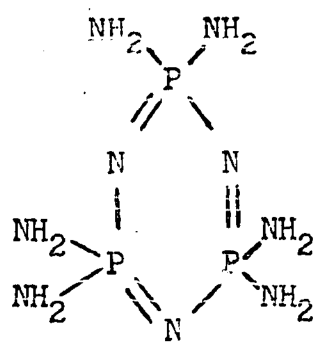


TRIPOLYPHOSPHORIC
ACID

Figure 1. Structural formulas of orthophosphoric acid and some polyphosphoric acids



PHOSPHORYL
TRIAMIDE



PHOSPHONITRILIC
HEXAAMIDE

Figure 2. Structural formulas of phosphoryl triamide and phosphonitrilic hexaamide

calcium fluoride, which indicates that the calcium is strongly complexed by the phosphate. Third, vitreous calcium metaphosphate has the property of forming a two-phase system when treated with an excess of water. One phase is a dilute solution of low-molecular-weight phosphates, and the other is a concentrated viscous phase, called "coacervate" by Brown and Lehr (1964), which contains the high-molecular-weight material. Condensed phosphate can react with urea to form urea condensed phosphates.

Conceivably, the phosphorus might be absorbed from the dilute solution without damaging the leaves, with gradual hydrolysis of high-molecular-weight polymers in the coacervate continuously supplying phosphorus to the dilute solution. The visous coacervate does not form immediately when water is added; it requires a period of several hours for development. The product could thus be applied as a suspension of the finely divided solid in water. Incorporation of silica decreases the formation of coacervate and increases the solubility of metaphosphate.

Ultraphosphates are even more complicated condensed phosphates, in that they have branching points in their molecular composition. Ultraphosphates generally decompose upon dissolution in water and are slowly soluble.

A third group of compounds that seemed to offer the possibility of reduced toxicity included the organic phosphates such as creatine phosphate, creatinine phosphate, adenosine phosphate, sugar phosphates, and phytate-, acetyl-, carbamyl- and glycine ethyl ester phosphate.

A fourth group of phosphorus compounds that was considered contains phosphorus-nitrogen bonds and phosphorus-nitrogen-phosphorus linkages. The nitrogen is present in the amide or imide form rather than as ammonium. These covalent compounds have a much lower ionic strength than orthophosphoric acid. One of these compounds, phosphoryl triamide, $PO(NH_2)_3$, is the phosphorus analog of urea. See Figure 2 for its structural formula. It is not appreciably ionized in water, but it gradually hydrolyzes with release of orthophosphate. Phosphonitrilic hexaamide, $P_3N_3(NH_2)_6 \cdot H_2O$, seems to be the next one in a sequence of compounds with respect to the speed of releasing orthophosphate groups through hydrolysis (Wakefield et al., 1971). It is a six-member ring compound with alternating phosphorus and nitrogen atoms in the ring. Two other compounds in this group are ammonium tri- and tetrametaphosphimate--$(NH_4)_3(PO_2NH_4)_3 \cdot H_2O$ and $(NH_4)_4(PO_2NH_4) \cdot 4H_2O$, respectively. These compounds would be expected to release their phosphate groups even more slowly than does phosphonitrilic hexaamide.

In the testing to be described, nearly all phosphorus compounds were applied in the ammonium form to avoid possible effects that different cations might have on phosphorus absorption. The plants were provided with an adequate nitrogen supply in the soil so that the effect of differing amounts of nitrogen supplied by various compounds could be neglected.

The chemicals prepared in the laboratory were synthesized shortly before application and were stored in a desiccator at 4^oC.

2. Preparation of materials

a. Inorganic phosphoric compounds   Dibasic ammonium orthophosphate, $(NH_4)_2HPO_4$, was prepared by diluting concentrated phosphoric acid and neutralizing it with ammonium hydroxide to pH 7.0. This product was regarded as a reference for evaluating the effectiveness of other phosphorus compounds.

Potassium pyrophosphate, $K_4P_2O_7$, was prepared according to Brown et al. (1963) by heating dipotassium phosphate, K_2HPO_4, slowly until frothing ceased. Then it was ignited at about 600^oC for 1 hour.

Ammonium pyrophosphate, $(NH_4)_4P_2O_7$. This compound was prepared by the ion-exchange method of Coates and Woodard (1964). (This method was used in all instances in which cations had to be exchanged to obtain the ammonium salt.)

Amberlite IR-120 resin in 30 x 3.5 cm columns was used. Before use, the resin was leached with the following reagents in the order named: 130 ml of a solution of one volume of concentrated hydrochloric acid and one volume of water; 170 ml of concentrated hydrochloric acid; water until the effluent was neutral; 150 ml of a solution of one volume of concentrated ammonium hydroxide solution and three volumes of water; and

300 ml of water. These liquids were passed through the column at a rate of approximately 5 ml/min.

A saturated solution of commercial tetrasodium pyrophosphate was run through the conditioned ion-exchange column at a rate of 1.5 ml/min. The ammonium pyrophosphate solution was collected, and the tetra-ammonium salt was precipitated by addition of an excess of absolute ethyl alcohol.

Ammonium tripolyphosphate, $(NH_4)_5P_3O_{10}\cdot H_2O$. Commercial anhydrous pentasodium tripolyphosphate was purified by four recrystallizations, using the method described by Van Wazer (1958, p. 648). A 13% solution of pentasodium tripolyphosphate hexahydrate (80 ml) was passed through the conditioned ion-exchange column at a rate of 1.5 ml/min. From the resulting solution, penta-ammonium tripolyphosphate was precipitated with ethyl alcohol.

Ammonium tetrapolyphosphate, $(NH_4)_6P_4O_{13}\cdot 6H_2O$. A mixture of 200.4 g of $PbCO_3$ and 115.3 g of 85% phosphoric acid was heated at 550°C for 12 hours according to a method given by Griffith (1964). The finely powdered lead tetrapolyphosphate was stirred with 1 liter of water, and 330 g of 17% $(NH_4)_2S$ was added slowly. The resulting PbS precipitate was filtered off. The ammonium tetrapolyphosphate was precipitated from the filtering with ethyl alcohol.

Ammonium monometaphosphate, NH_4PO_3, was prepared according to Kiehl and Hill (1927) by metathesis of $Pb(PO_3)_2$ with $(NH_4)_2S$. The PbS was filtered off, and the ammonium monometaphosphate was precipitated from the filtrate with ethyl alcohol. Van Wazer (1958, p. 682) doubts that the monometaphosphate exists and suggests that it is a trimer or a modification of the tetramer.

Ammonium trimetaphosphate, $(NH_4)_3P_3O_9$. Anhydrous trisodium trimetaphosphate was prepared by heating sodium dihydrogen orthophosphate for 5 hours at 530°C. The cake was extracted with water and filtered to remove the higher insoluble phosphates. The ammonium trimetaphosphate was precipitated with ethyl alcohol. An oil formed, which quickly solidified as the monohydrate, $Na_3P_3O_9 \cdot H_2O$. A 20% solution of trisodium trimetaphosphate (50 ml) was passed through the conditioned ion-exchange column. From the collected solution, triammonium trimetaphosphate was precipitated with ethyl alcohol.

Ammonium tetrametaphosphate, $(NH_4)_4P_4O_{12}$. Tetrasodium tetrametaphosphate was prepared according to a slight modification of the method by Griffith (1956). A quantity of 34.5 g of NaH_2PO_4 was mixed with 28.8 g of 85% orthophosphoric acid contained in a platinum dish. The dish was placed in a cool muffle furnace, and the temperature was raised to 500°C during a period of 1 hour. This temperature was maintained for 1 hour. Then the dish was transferred to another furnace preheated to 300°C, and the solution was stirred for 2 to 3 minutes to hasten the crystallization. The clear melt crystallized within 12 to 16 hours. The material was then ground to a powder and washed with as many milliliters of water as there were grams of product. The sample was filtered on a Büchner funnel and washed with 100 ml of acetone for each 50 grams of product. An aqueous solution of the $Na_2H_2(PO_3)_4$ was neutralized to pH 7.0 with sodium carbonate, and methanol was added to crystallize the $Na_4P_4O_{12} \cdot 10H_2O$.

A 13% solution of tetrasodium tetrametaphosphate (60 ml) was passed through the conditioned ion-exchange column. Tetra-ammonium tetrametaphosphate was precipitated with ethanol from the collected solution.

Potassium metaphosphate, KPO_3, was prepared by heating KH_2PO_4 in a muffle furnace at 875°C for 3 hours and then quenching the melt in air (Egan and Wakefield, 1960). The product was ground to pass a 300-mesh sieve.

Calcium metaphosphate, $Ca(PO_3)_2$. Reagent-grade monocalcium phosphate monohydrate was fused in a platinum dish at about 1100°C, and the melt was quenched in water. This vitreous material, essentially a noncrystalline, long-chain polyphosphate, was ground to pass a 300-mesh sieve.

Calcium (Si) metaphosphate was prepared by fusing a mixture of pure vitreous metaphosphate, prepared according to the description given above, and 2.7% SiO_2.

Ultra-high-analysis NH_2-P-O reaction products. Three gas-phase reaction products were kindly supplied by Dr. G. L. Terman, Agronomist, Soils and Fertilizer Research Branch, National Fertilizer Development Center, Tennessee Valley

Authority, Muscle Shoals, Alabama. The materials were prepared according to a description by Terman and Allen (1969) by metering precalculated amounts of gaseous NH_3, P, and air into a reactor. Table 8 lists the properties of three different compounds (G. L. Terman, personal communication, 1970).

Table 8. Properties of three NH_3-P-O reaction products

Product number	Fertilizer grade	Water soluble, %	Reaction temperature, °C	Retention time, sec
149	15-75-0	96	538 first stage 793 second stage	2.0
157	15-76-0	90	538	2.5
165	14-74-0	91	732	1.0

Urea ammonium ortho- and polyphosphate were obtained through the courtesy of Dr. A. P. Edwards, Division of Agricultural Development, Tennessee Valley Authority, Muscle Shoals, Alabama. These products contain, respectively, 12.4 and 13.9% phosphorus.

Condensed urea phosphate. Urea and P_2O_5 were mixed in the molar ratio of 4:1 at 80°C according to the method described by Bozadzhiev and Vol'fkovich (1967).

Na-Churs product. This commercial liquid fertilizer was kindly made available by Mr. J. Goddard, General Manager of Na-Churs Plant Food Co., Red Oak, Iowa. The composition is

9-18-9. The principal components mixed to produce the fertilizer were given as phosphoric acid, urea, potassium hydroxide, and ammonium hydroxide. The fertilizer contains, in addition, minute amounts of chelated iron and manganese and some sulfate (J. Goddard, personal communication, 1971).

Ammonium polyphosphate. A commercial product of Allied Chemical Corporation (Wagner, 1971) was used in unaltered form. At least 50% of the phosphorus is in the polyphosphate form.

Choline phosphate. Choline is an organic nitrogen compound and a strong base. It was used to neutralize orthophosphoric acid before application to the leaves.

Guanidine phosphate. Guanidine, $NH{:}C(NH_2)_2$, is a crystalline organic base of strength equivalent to sodium hydroxide. The commercial product, guanidine carbonate, is very stable, and was reacted with phosphoric acid to produce the neutral phosphate salt.

Guanylurea phosphate. Guanylurea is another organic nitrogen compound with basic properties. Guanylurea sulfate, $(NH_2C{:}NHNHCONH_2)_2 \cdot H_2SO_4$, the commercial form employed, was treated with $Ba(OH)_2$ to precipitate the sulfate. The resulting solution of guanylurea was then neutralized to pH 7.0 with orthophosphoric acid.

Phosphoryl triamide, $PO(NH_2)_3$, was kindly supplied, as were the next three compounds, by Dr. Z. T. Wakefield, Chief, Fundamental Research Branch, Division of Chemical Development, Tennessee Valley Authority, Muscle Shoals, Alabama. This product has a reported pH of 6.0 (Van Wazer, 1958; Wakefield et al., 1971) and is stable in dry air but loses ammonium after being exposed for about a month in moist air. It is the phosphorus analog of urea and is not appreciably ionized in water.

Phosphonitrilic hexaamide monohydrate, $P_3N_3(NH_2)_6 \cdot H_2O$, is readily soluble in water, in which it hydrolyzes slowly according to the following sequence: phosphoryl triamide, diamidophosphate, monoamidophosphate, and diammonium orthophosphate plus free ammonium.

Ammonium trimetaphosphimate, $(NH_4)_3(PO_2NH)_3 \cdot 0.3H_2O$, was obtained as the sodium salt, and the sodium cations were exchanged for ammonium with the help of the ion-exchange resin column described previously. It hydrolyzes slowly and according to a complex path (Van Wazer, 1958, p. 840).

Ammonium tetrametaphosphimate, $(NH_4)_4(PO_2NH)_4 \cdot 4H_2O$, is a cyclic compound and is expected to be even more resistant to hydrolysis than the trimetaphosphimate, which also is a ring compound.

b. Organic phosphorus compounds   Creatine phosphate. The commercial product was in the sodium form, $C_4H_8N_3Na_2O_5P \cdot 6H_2O$, and was passed through an ammonium-saturated ion-exchange column to prepare the ammonium salt.

Creatinine phosphate. The commercial sodium salt was changed into an ammonium salt by passing the solution through an ammonium-saturated ion-exchange column.

Adenosine triphosphate. The commercial barium salt was dissolved and treated with an equimolar amount of ammonium sulfate. The precipitated $BaSO_4$ was filtered off. Adenosine triphosphate is a high-energy phosphate and is a natural constituent of plants.

Glucose-6-phosphate. The commercial barium salt was changed to an ammonium salt by adding an equimolar amount of $(NH_4)_2SO_4$ in solution and filtering off the resulting precipitate of $BaSO_4$.

Fructose-1,6-diphosphate. The commercial product was the monocalcium salt, which was passed through the ammonium-saturated ion-exchange column to obtain the ammonium salt.

Acetyl phosphate. To obtain the ammonium salt, the commercial silver salt was treated with ammonium chloride, and the resulting precipitate of AgCl was filtered off.

Carbamyl phosphate. The commercial salt was in the lithium form and was passed through the ammonium-saturated ion-exchange column to obtain the ammonium salt.

Ammonium phytate. Calcium phytate is a natural constituent of plants. It is a concentrated source of phosphorus and is highly ionic. The molecular configuration consists of a six-carbon ring with one phosphate group at each carbon atom. Five grams of calcium phytate was dissolved in 100 ml of water with the aid of a hydrogen-saturated cation-exchange resin. The solution was passed through the ammonium-saturated cation-exchange resin column.

Glycine ethyl ester phosphate. The commercial product was brought to pH 7.0 with ammonium hydroxide before application.

3. Identification and quality control of the products

X-ray diffraction patterns were made of each batch of condensed phosphate prepared in the laboratory. The patterns were compared with the ones published by Lehr et al. (1967) and Coates and Woodard (1964). This technique made it possible to detect contamination of the products with crystalline phosphates other than the one of interest when the concentration of the contaminant amounted to a few percent.

Table 9 shows the nitrogen, phosphorus, potassium, calcium, magnesium, and sodium analyses of five condensed phosphates prepared for use in the first experiment. The sodium content of the end-product never exceeded 0.4% and was in most cases significantly lower. This finding indicates that a good exchange of sodium for ammonium was obtained through the ion-exchange-column technique.

The phosphorus and nitrogen contents were always within 1% of the theoretical value. Values below the theoretical may be a consequence of making the analysis on compounds that had not been dried at elevated temperatures.

Table 9. Chemical analysis of five condensed phosphates as prepared for use in the experiments

Phosphorus compound	Chemical formula	Nitrogen	
		Analysis	Theoretical
		---------%---------	
Ammonium pyrophosphate	$(NH_4)_4P_2O_7$	23.45	22.77
Ammonium tripolyphosphate	$(NH_4)_5P_3O_{10} \cdot H_2O$	18.11	19.39
Ammonium tetrapolyphosphate	$(NH_4)_6P_4O_{13} \cdot 6H_2O$	14.78	15.33
Ammonium monometaphosphate	NH_4PO_3	14.95	14.44
Ammonium tetrametaphosphate	$(NH_4)_4P_4O_{12}$	15.02	14.44

Phosphorus					
Analysis	Theo-retical	Potassium	Calcium	Magnesium	Sodium
%					
24.77	25.17	0.0160	0.0022	0.0034	0.020
25.04	25.73	0.0033	0.0012	0.012	0.000
21.03	22.60	0.0043	0.0020	0.004	0.401
31.35	31.93	0.0180	0.0011	0.009	0.009
32.43	31.93	0.0180	0.0018	0.008	0.213

4. Adjustment of pH of phosphorus solutions

If the pH of the solution was lower than 7.0, it was adjusted by adding ammonium hydroxide. If the pH was higher than 7.0, a hydrogen-saturated cation-exchange resin was added in small quantities until the pH was slightly below 7.0. The final adjustment of pH was then made by adding dilute ammonium hydroxide.

5. Methods

a. Delineation of fixed leaf areas It was considered important to obtain quantitative as well as qualitative information on the various phosphorus compounds to be tested in the screening experiments. Therefore, a technique of applying a predetermined quantity of phosphorus to a fixed leaf area was developed.

A leaf area of 1.13 cm^2 was delineated with a waxy material. A predetermined quantity of phosphorus was applied in solution in a volume of 25 μl and was spread out over the entire surface within the waxy circle by means of a glass rod with a fire-polished tip. The glass rod was treated with "siliclad" to make it water repellent.

Experiments were done to find a material that would be easily applied, would prevent the solution from spreading beyond the desired area, and would not damage the leaf. Different paraffins, vaseline, lanolin, and combinations of these substances were tried The best product tested was a mixture of 75% paraffin with a melting point of 52°C (Fisher Scientific Co.) and 25% lanolin. The mixture was applied with a dull No. 7 cork borer. The borer was dipped to a depth of about 1 cm in the melted mixture (kept at about 100°C) for 1 to 2 seconds and was then pressed very slightly on the leaf surface while turning the borer through an arc of about 90°. During this process, the leaf was supported by a thick layer of felt material.

b. Leaf sampling   A cork borer with a diameter slightly greater than that of the ring enclosing the treated area was used to cut out the treated area for analysis. The leaf discs were shaken vigorously for 5 minutes in 10 ml of 0.1% Tween-80 solution in 2-ounce glass bottles. The leaf discs were then immediately transferred to other bottles and dried at 65°C. The phosphorus removed from the cut leaf discs was determined as a measure of the unabsorbed phosphorus. The washed leaf discs were also analyzed for total phosphorus. By use of appropriate controls, it was possible to determine how much of the added phosphorus had been absorbed and how much of the absorbed phosphorus had been translocated out of the leaf discs.

c. Damage estimates   Two parameters were used to describe damage done to the leaves by the phosphorus compounds. First, the damaged area was visually estimated and expressed as a percentage of the total treated area. Secondly, the damaged area was rated according to the following system as regards appearances:

0 = no damage

1/2 = very slightly discolored and noticeable only by holding the leaf to the light

1 = discolored but apparently not dead

2 = mostly dark in color and apparently dead, sometimes with small areas light tan to gray and obviously dead

3 = mostly or entirely light tan to gray and obviously dead

In the tables in which the results are reported, two numbers for the damage rating signify about equal areas of both degrees of damage. If one of the numbers is underlined, about two-thirds of the total damaged area has the rating indicated by that number.

d. Determination of total phosphorus   Ten ml of 1% magnesium acetate solution containing 0.2% Tween-80 was added to the samples, and the solution was then evaporated to dryness. The samples were ashed by putting the bottles in a muffle furnace and heating them slowly to 500°C. This temperature was maintained for 2 hours. After the furnace had cooled, the bottles were removed, and the ash was moistened with 5 ml of 0.5 N H_2SO_4, which was added with an acid-resistant pipettor. The samples were placed on a steam plate for 3 minutes, which helped to dissolve the salts. Then 25 ml of distilled water was added with a large syringe-type automatic pipettor, and then 5 ml of an ascorbic acid-ammonium molybdate solution was added (Watanabe and Olsen, 1965). Ten minutes later, the transmit· ncy was measured with a photoelectric colorimeter equipped with a 720-millimicron filter.

The amount of phosphorus per sample was calculated by reference to a calibration curve plotted from the results obtained with standards containing 0, 2.5, 5, 10, 15, 20, and 30 µg of phosphorus per sample. To prepare this graph, 0, 0.5, 1, 2, 3, 4, and 6 ml aliquots of a standard phosphate solution containing 5 ml of the phosphorus stock solution per 10 ml were pipetted into bottles and taken through the digestion procedure with each series of 30 to 40 samples.

Samples which contained more than 25 µg of phosphorus were diluted 3, 6, 10, or 20 times by taking an aliquot from the sample after the water had been added and by adding water to the aliquot. The dilute sulfuric acid to dissolve the salt was then made stronger by as many times as the dilution factor. The standard series was also made the same factor higher in phosphorus and was taken through the same dilution procedure as the samples.

e. Reagents   Sulfuric acid, 0.5 N: To about 3 liters of water was added 56 ml of concentrated (36 N) sulfuric acid. The solution was diluted to 4 liters with water.

Ammonium molybdate-antimony potassium tartrate (reagent A): A quantity of 13.44 g of ammonium molybdate was dissolved in

250 ml of water, and 0.3256 g of antimony potassium tartrate was dissolved in 100 ml of water. Both solutions were added to 920 ml of 5 N sulfuric acid, and the mixture was diluted to 2 liters with water and was mixed thoroughly. This reagent was stored in a pyrex glass bottle in a dark, cool place.

Ascorbic acid solution (reagent B): A quantity of 1.18 g of ascorbic acid was dissolved in 200 ml of reagent A, and the solution was mixed thoroughly. This reagent was prepared shortly before use, and any excess was discarded after a few hours. The solution was kept covered to prevent its oxidation by air.

Phosphorus stock solution: A quantity of 0.4388 g of potassium dihydrogen phosphate (KH_2PO_4) was dissolved in water, and the volume was brought to 1 liter with water in a volumetric flask. This solution contains 100 μg of phosphorus per milliliter.

B. Phosphorus Screening Experiment No. 1

1. Introduction

From the literature study and the results obtained by Hanley and Phillip (see Section III), it appears that orthophosphate is obserbed rapidly by the leaves of the plants tested, but that its toxicity limits the quantity which can be applied in one spray.

Neutralization of phosphoric acid with inorganic or organic bases or adding urea or sucrose do not reduce the toxicity to an acceptable degree. Screening experiments were therefore undertaken in an attempt to find compounds that would supply greater amounts of phosphorus without causing damage. Compounds were selected for testing on the basis of their ionic character, their susceptibility to hydrolysis and the rate at which they released phosphate. Also included were compounds of orthophosphate with organic bases that had not been tested previously.

2. Procedure

Soybeans, variety Hark, were planted in the greenhouse on June 12, 1970, in plastic vessels containing 1 kg of a mixture of two parts of sandy loam soil, one part of peat, and one part of sand. Monobasic potassium phosphate and ammonium nitrate were mixed with the soil in quantities to supply 200 ppm of nitrogen, 100 ppm of phosphorus, and 125 ppm of potassium. Funk's G-4444 corn was planted on June 17 in vessels similarly prepared. All vessels received 5 ml of an iron-chelate[1] solution of 2.8 g per liter on June 29 because the plants, especially corn, showed some iron chlorosis. On July 5, all pots received 50 ppm of N in the form of ammonium nitrate. This treatment was repeated three more times at intervals of about 14 days.

Quantities of 0, 1, and 3 μmols of phosphorus in a 25-μl

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[1]Iron tetrine, distributed by Glyco Products Co., Inc., Empire State Building, New York, N.Y.

volume of solution of the compounds listed in Table 10 were applied at random to three circles with an area of 1.13 cm^2 on the youngest mature leaf of corn and soybean plants on July 31 through August 5. On the corn plants the three circles were at a distance of 10 to 15 cm from each other on the same leaf. The middle circle was on one side of the main vein, and the other two were on the other side. With soybeans, the three treatments were applied to the individual leaflets of one trifoliate leaf. A micropipet was used to make the 25-µl applications. At the time of application, 25-µl aliquots of the solution were pipetted into 50-ml beakers in three replications to be used for the determination of the exact quantity of applied phosphorus. All solutions contained 0.25% Tween-80.

The treatments were applied in nine replications. The plants were arranged on benches of the Agronomy greenhouse according to a completely randomized block design.

Periodically the greenhouse was fumigated with Parathion gas, and the plants were sprayed with Morestan to keep the thrips, lice, and red spider mites under control.

Estimates of damage to the leaves were made 5 days and 17 days after application of the solutions, and leaf samples were taken 18 days after the phosphorus compounds were applied, according to procedures described in parts A5b and 5c of this section.

Table 10. Absorption and translocation of phosphorus applied in various forms to leaves of corn, and damage to the leaves from the applications in Experiment 1

Phosphorus compound	pH	P applied, $\mu g/cm^2$	Estimates of After 5 days Rating	Area
Inorganic phosphorus compounds				
Potassium pyrophosphate	6.8	28	0	0
		85	0	0
Ammonium pyrophosphate	6.9	29	0	0
		85	2	1
Ammonium tripolyphosphate	7.1	28	0	0
		82	1	8
Ammonium trimetaphosphate	6.2	34	1	8
		105	1,2	17
Ammonium tetrametaphosphate	6.9	27	0	0
		81	1,2	18
Potassium metaphosphate	7.0	27	0	0
		82	0	0
Calcium metaphosphate	7.0	18	0	0
		53	1	2
Calcium (Si) metaphosphate	7.0	14	1	6
		40	1	5
Ultraphosphate No. 157	7.0	28	1	8
		82	1,2	19
Ultraphosphate No. 165	7.0	29	1	1
		83	1	15
Ultraphosphate No. 149	7.0	29	0	0
		83	1	2
Urea ammonium polyphosphate	6.3	28	1	1
		84	1,2	16
Condensed urea phosphate	7.0	28	1	3
		84	1	17

[a]See Section IV-A5c (p. 111) for a description of the code used to describe the damage to the leaves.

leaf damage[a].				
After 17 days		Increase from the 5th to the 17th day in %	P absorbed as % of P applied	P trans-located as % of P absorbed
Rating	Area			
1	18	>200	84	99
1	19	>200	85	88
0	0	0	82	79
1,3	15	>200	87	74
0	0	0	83	66
1	5	-38	94	68
1	4	-50	90	77
1,3	24	41	94	85
0	0	0	60	63
2,3	44	144	-	-
0	0	0	38	50
0	0	0	40	77
0	0	0	26	88
0	0	-100	33	94
0	0	-100	15	90
0	0	-100	27	90
0	0	-100	68	69
1,2	11	-42	88	50
0	0	-100	79	66
2	27	80	84	80
1,2	15	>200	62	79
1,2	12	>200	85	74
1,2	15	>200	94	70
1	14	-13	93	72
0	0	-100	62	76
1,2	31	82	62	59

Table 10. (Continued)

Phosphorus compound	pH	P applied, $\mu g/cm^2$	Estimates of	
			After 5 days	
			Rating	Area
		Orthophosphoric acid neutralized		
Choline phosphate	7.0	28	1,2	16
		83	1	18
Guanidine phosphate	7.0	28	1,2	93
		85	3	160
Guanylurea phosphate	7.0	29	0	0
		84	1	12
			Organic phosphorus	
Creatine phosphate	7.0	19	0	0
		65	1	1
Adenosine triphosphate	6.9	9	0	0
		27	1	1
Glucose-6-phosphate	7.0	28	0	0
		88	2	3
Acetyl phosphate	7.0	29	1	17
		92	1	12
Carbamyl phosphate	7.0	31	1	4
		93	1	1
Ammonium phytate	7.0	25	1,2	14
		77	1,3	67
Glycine ethyl ester phosphate	7.0	29	0	0
		88	1,2	24

leaf damage[a]				
After 17 days		Increase from the 5th to the 17th day in %	P absorbed as % of P applied	P trans-located as % of P absorbed
Rating	Area			
with organic nitrogen bases				
1	14	-13	99	92
2,3	68	>200	-	-
3	>100	>200	-	-
3	>500	>200	-	-
0	0	0	38	86
0	0	-100	17	76
compounds				
0	0	0	77	78
1	10	>200	83	82
0	0	0	49	44
1	1	0	46	61
0	0	0	87	87
1	11	>200	94	77
0	0	-100	82	63
1	1	-92	90	63
1	20	>200	93	84
1,2	30	>200	87	89
1	11	-21	70	80
2,3	70	5	-	-
0	0	0	94	89
2	11	-54	99	97

3. Results and discussion

a. Environmental conditions during the experiment

July, August, and September of 1970 were exceptionally warm, with outside temperatures frequently over 100°F. Actions taken to keep the greenhouse as cool as feasible were covering the roof with whitewash, use of window fans, and use of a water sprinkler system under the benches. Nevertheless, the temperatures in the greenhouse rose frequently to 105 to 107°F.

At the time of this experiment, the roof of the greenhouse had many leaks, which caused dripping on some of the plants during rain showers. Some very low phosphorus analyses were eliminated for this reason before calculating the means.

b. Corn Table 10 gives the amount of applied phosphorus, the pH of the solution, the estimates of damage to the leaves, and the absorption of phosphorus from the various compounds used. The values are means of four replications. Under the estimates of leaf area damaged, the values given are the percentage of the treated area which showed damage. The damage rating ranges from 0 for no visual damage to 3 for obviously dead leaf tissue (see A5c for the detailed rating scale). Phosphorus absorption is expressed as a percentage of the quantity of applied phosphorus.

Because it is not known if the phosphorus is absorbed in the orthophosphate form or in some other form, the possibility exists that certain phosphorus compounds may be absorbed but cannot be metabolized by the plants. A measure of the mobility of the phosphorus in the plant thus may provide an indication of the availability of the absorbed phosphorus for plant metabolism. To obtain such information, the leaf discs were also analyzed for total phosphorus. From the total phosphorus in the leaf disc, the total phosphorus added, the phosphorus washed off at the end of the test period, and the phosphorus present in the control, it was possible to calculated the translocation of absorbed phosphorus from the leaf disc. The translocation is expressed in Table 10 as a percentage of the phosphorus absorbed from the solution applied to the leaf disc. Table 11 gives the analyses made on the leaf discs that were treated only with a solution containing 0.25% Tween-80. These values were used as controls in the calculations.

Table 11. Means of the phosphorus content of the leaf washings and leaf discs of the control treatment in Experiment 1

	Phosphorus per 1.8 cm^2 of leaf surface, μg	
Crop	Leaf washings	Leaf discs
Corn	1.55	11.6
Soybeans	1.42	23.2

Some treatments produced so much damage that it was not considered worthwhile to make the analyses. Such instances are indicated by a dash (-) in the tables.

In the following discussion on the comparison of the various compounds applied to corn, three parameters will be taken into consideration, namely, the damage, the absorption, and the translocation.

Of the inorganic phosphates, tripolyphosphate appeared to be the best performer, with only 5% damage and 94% absorption. The long-chain polyphosphates, potassium and calcium metaphosphates, showed no damage at all, but their absorption was significantly lower than that of the condensed phosphates with lower molecular weights. These compounds were applied as a suspension because of their low solubility, and even 30 days after their application the particles were clearly visible on the leaf surface. Adding silicon during the preparation of calcium metaphosphate to shorten the chain length decreased the phosphorus absorption. The translocation of phosphorus absorbed from these long-chain polyphosphates, however, was just as good as that of phosphorus absorbed from the other condensed phosphates.

Urea can be applied at a rather high concentration to foliage and is well absorbed. The combination of urea and polyphosphate gave a high absorption but also more damage than tripolyphosphate alone. The condensed urea phosphate produced considerable leaf damage, perhaps as a consequence of the large amount of urea or the biuret that may have been formed during manufacture of the product. The relatively low absorption of 62% might be due to occurrence of a large percentage of the phosphorus in long chains.

Neutralizing orthophosphoric acid with nitrogen-containing organic bases resulted in leaf damage or low absorption. The extensive damage and the considerable increase in damage from the first observation to the second indicate the toxicity of the product.

Among the organic phosphorus compounds, carbamyl phosphate seemed especially toxic. Adenosine triphosphate was neither absorbed well nor translocated well. Acetyl phosphate was absorbed well but was not translocated well. Glucose-6-phosphate and glycine ethyl ester phosphate appear to be the best performing organic phosphates. Glycine ethyl ester phosphate caused a significant amount of discoloration of the leaves (given damage rating 1) directly after application, but the discoloration disappeared partly or completely later on.

c. Soybeans The estimates of leaf damage and phosphorus absorption for the soybeans are given in Table 12. In general, soybeans showed more damage than corn at a given concentration of a particular compound. The phosphorus absorption was similar to that obtained with corn, but the translocation was significantly lower for most compounds. The two crops, corn and soybeans, certainly behaved differently with respect to certain phosphorus compounds.

Promising inorganic phosphates for soybeans appeared to be ammonium tetrametaphosphate, which caused less damage on soybeans than on corn at similar concentrations, and

Table 12. Absorption and translocation of phosphorus applied in various forms to leaves of soybeans, and damage to the leaves from the applications in Experiment 1

Phosphorus compound	pH	P applied, µg/cm²	Estimates of: After 5 days Rating	Area
Inorganic phosphorus compounds				
Potassium pyrophosphate	6.8	28	0	0
		85	1	9
Ammonium pyrophosphate	6.9	29	0	0
		85	2,3	50
Ammonium tripolyphosphate	7.1	28	0	0
		82	2	41
Ammonium trimetaphosphate	6.2	34	1	9
		105	2	53
Ammonium tetrametaphosphate	6.9	27	0	0
		81	1	10
Potassium metaphosphate	7.0	27	0	0
		82	0	0
Calcium metaphosphate	7.0	18	0	0
		53	0	0
Calcium (Si) metaphosphate	7.0	14	0	0
		40	0	0
Ultraphosphate No. 157	7.0	28	0	0
		82	1	11
Ultraphosphate No. 165	7.0	29	0	0
		83	1	11
Ultraphosphate No. 149	7.0	29	0	0
		83	2	20
Urea ammonium polyphosphate	6.3	28	1	3
		84	3	60
Condensed urea phosphate	7.0	28	0	0
		84	2	25

[a]See Section IV-A5c for the code of rating used to describe the damage to the leaves.

leaf damage[a]				
After 17 days		Increase from the 5th to the 17th day in %	P absorbed as % of P applied	P translocated as % of P absorbed
Rating	Area			
0	0	0	74	77
3	50	>200	-	-
0	0	0	80	57
1.3	50	0	-	-
0	0	0	85	60
1,3	50	22	95	39
1,2	4	-56	81	63
2	50	-6	-	-
1	5	>200	82	48
1,2	11	10	83	41
0	0	0	64	83
0	0	0	63	90
0	0	0	37	75
0	0	0	30	90
0	0	0	27	64
0	0	0	45	80
0	0	0	88	36
1	11	0	91	22
0	0	0	90	48
1	1	-91	87	29
1	1	>200	92	45
2	42	110	-	-
0	0	-100	88	73
3	52	-13	-	-
0	0	0	66	53
3	22	-12	-	-

Table 12. (Continued)

Phosphorus compound	pH	P applied, $\mu g/cm^2$	Estimates of After 5 days Rating	Area
		Orthophosphoric acid neutralized		
Choline phosphate	7.0	28	1,2	10
		83	2,3	72
Guanidine phosphate	7.0	28	3	>300
		85	3	>500
Guanylurea phosphate	7.0	29	3	52
		84	3	43
			Organic phosphorus	
Creatine phosphate	7.0	19	0	0
		65	2,3	27
Adenosine triphosphate	6.9	9	0	0
		27	1	3
Glucose-6-phosphate	7.0	28	1,2	3
		88	2	44
Acetyl phosphate	7.0	29	1	3
		92	2,3	68
Carbamyl phosphate	7.0	31	1	3
		93	0	0
Ammonium phytate	7.0	25	0	0
		77	1	7
Glycine ethyl ester phosphate	7.0	29	1	6
		88	3	88

leaf damage				
After 17 days		Increase from the 5th to the 17th day in %	P absorbed as % of P applied	P trans-located as % of P absorbed
Rating	Area			
with organic nitrogen bases				
3	4	-60	95	66
3	60	-17	-	-
3	>400	100	-	-
3	>1000	100	-	-
3	100	92	-	-
3	126	193	-	-
compounds				
0	0	0	76	75
3	18	-33	84	68
0	0	0	52	67
1	5	67	58	55
1	2	-33	94	99
3	38	-14	-	-
1	1	-67	93	55
3	210	>200	-	-
1	1	-67	94	68
3	45	>200	-	-
0	0	0	93	50
1	9	29	92	38
1,2	11	83	96	60
3	72	-18	-	-

ultraphosphate No. 165.

The use of organic bases to neutralize orthophosphoric acid did not appear to be the solution to the problem of damage to the leaves of soybeans. All three of the bases tested were relatively toxic.

Ammonium phytate appeared to be the best performing organic phosphate. This compound also gave significantly less damage on soybeans than on corn, which is surprising, because it is a natural constituent of corn.

In many instances, the percentage absorption of the phosphorus was higher with the 3 μmol application than with the 1 μmol application. The explanation for this observation is not clear.

C. Phosphorus Screening Experiment No. 2

1. Introduction

A second screening experiment was conducted that included compounds which damaged less than 10% of the leaf area and which were absorbed well in the first experiment as well as some other compounds that had not been applied before.

To improve the differentiation among compounds on the basis of phosphorus absorption, it was decided to sample the leaves 10 days after application of the phosphates instead of 18 days as was done in the first experiment. Including a longer sampling term of several weeks was considered important with respect to judging possible long-term damage to the leaves.

In the first experiment, the phosphorus analyses on the leaf discs showed a larger variability among replications with corn (average C.V. was 28%) than with soybeans. This observation seemed to be a consequence of an influence of phosphorus absorbed at one place on the phosphorus in leaf discs lower on the leaf and on the same side of the main vein. Consequently, no double applications on the same side of the main vein were made in this and following experiments.

2. Procedure

Soybeans, variety Hark, were planted on June 12, 1971, in number 10 cans, which contained 3.2 kg of soil mixture. The soil was fertilized with 140 ppm of nitrogen, 70 ppm of phosphorus, and 90 ppm of potassium in the form of monobasic potassium phosphate and ammonium nitrate. Funk's G-4444 corn was planted on June 18. Three seeds of both crops were planted per pot, and after emergence, the stand was reduced to one plant per pot.

All plants received an application of iron-chelate solution on June 29. On August 2 and 10, the corn plants received 250 mg of ammonium nitrate per pot.

Applications of 25-μl volumes of solution containing 3 μmol of phosphorus in the case of inorganic compounds and 1 μmol in the case of organic phosphates were made to leaf circles on July 13 and 15. In this experiment, 25-μl disposable micropipets, manufactured by Drummond Scientific Co., 500 Parkway, Broomall, Pennsylvania, were used to make the applications.

In the first experiment, it was learned that the variability in phosphorus analyses among blanks on the different plants was smaller than 10%, which justified considering the control, 0.25% Tween-80, as an independent treatment instead of having a control treatment on each plant.

In this experiment, there were two treatments per plant. With corn, the treatments were applied on opposite sides of of the main vein of the youngest mature leaf. With soybeans, the treatments were applied to separate leaflets. The treatments were applied in a randomized block design with ten replicates. There were two control treatments in each block.

The pH of nearly all solutions was brought to 7.0, but no efforts were made to bring the pH down when pH 7.0 was exceeded during exchange of ammonium for the original cation in the phosphate compound.

Because of their low solubility, potassium and calcium metaphosphates were applied as a suspension. Carboxymethyl cellulose ether (sodium salt) was used at a concentration of 0.5% to help keep the particles suspended. Tests were done to determine that carboxymethyl cellulose ether did not affect the absorption of the phosphorus or the removal of the unabsorbed phosphorus from the leaf surface by washing.

3. Results and discussion

Table 13 gives the amounts of phosphorus in the leaf washings and the leaf discs of the control treatments. These values were used to correct the phosphorus analyses of the phosphorus treatments in calculating the percent absorption and translocation.

Table 14 gives the means of the estimates of damage to the leaves, the phosphorus absorption, expressed as a percentage of the applied phosphorus, for corn. Table 15 gives the analogous data for soybeans.

In general, the leaf damage was less in this experiment than in the first experiment. This result may be a consequence of the much lower temperatures that prevailed in the greenhouse during this experiment than during the first experiment.

a. Corn No clear distinction in performance could be made between orthophosphate, pyrophosphate, tripolyphosphate, tetrametaphosphate, and the commercial mixture of ammonium polyphosphates. None of these compounds caused much damage at the concentration of 3 μmol/1.13 cm^2, and all compounds were well absorbed and translocated by the leaves. The long-chain polyphosphates were not absorbed as well as the others mentioned, but the translocation of the absorbed phosphorus was just as good as it was with the other condensed phosphates. These results correspond very well with those obtained in Experiment 1. Calcium metaphosphate was applied

Table 13. Means of the phosphorus content of the leaf washings and leaf discs of the control treatment in Experiment 2

Length of experiment, days	Phosphorus per 1.8 cm^2 of leaf, μg			
	Corn		Soybeans	
	Washings	Discs	Washings	Discs
10	0.86	13.0	0.77	18.3
32	0.93	18.0	0.84	26.7

at a lower pH to see if this would increase uptake, but the results indicate that this treatment was not effective.

Ultraphosphates No. 157 and 149 produced much damage in the long-term experiment, and No. 165 had a low absorption. Why the absorption of No. 165 in this experiment was so much lower than in Experiment 1 is not clear.

Urea ammonium orthophosphate performed equally as well as regular orthophosphate. It is not clear why urea ammonium polyphosphate caused more damage than the urea orthophosphate.

The absorption of guanyl urea phosphate was higher than in the first experiment, but it was still not as good as absorption of the other compounds.

All the organic phosphorus compounds except adenosine triphosphate were absorbed and translocated very well, and they caused no damage at the low concentration applied.

Table 14. Absorption and translocation of phosphorus applied in various forms to leaves of corn, and damage to the leaves from the applications in Experiment 2

Phosphorus compound	pH	P applied, $\mu g/cm^2$	Results after: Estimate of leaf damage[a] Rating	Results after: Estimate of leaf damage[a] Area
Inorganic phosphorus compounds				
Ammonium orthophosphate	7.0	76	½,1	1
Ammonium pyrophosphate	7.0	99	1	1
Ammonium tripolyphosphate	7.9	76	1	1
Ammonium monometaphosphate	7.0	80	1,2	5
Ammonium tetrametaphosphate	7.0	79	0	0
Ammonium polyphosphate	7.0	79	1,3	4
Potassium metaphosphate	6.6	57-79	2	4
Calcium metaphosphate	4.1	36-60	1	1
Calcium (Si) metaphosphate	4.2	40-69	0	0
Ultraphosphate No. 157	7.0	84	1,2	10
Ultraphosphate No. 165	7.0	78	1	5
Ultraphosphate No. 149	7.0	77	1,2	1-5
Urea ammonium orthophosphate	7.8	80	1	1
Urea ammonium polyphosphate	7.0	82	2,3	29
Guanyl urea phosphate	7.2	21	1	1

[a]See Section IV-A5c for a description of the code used to describe the damage to the leaves.

10 days		Results after 32 days			
		Estimate of leaf damage			
P absorbed as % of P applied	P trans-located as % of P absorbed	Rating	Area	P absorbed as % of P applied	P trans-located as % of P absorbed
95	97	1	1	99	91
86	94	1	3	91	91
90	96	1	3-10	92	88
85	99	1,2	5-50	-	-
78	96	0	0	-	-
76	82	1,2	4	82	83
31	95	2	4	29	85
20	90	1	1	20	90
20	90	0	0	6	90
77	84	1,2	55	-	-
38	78	1,3	10	-	-
72	90	2	15	-	-
97	98	1	1	99	85
-	-				
46	86	1	1	-	-

Table 14. (Continued)

Phosphorus compound	pH	P applied, $\mu g/cm^2$	Results after	
			Estimate of leaf damage[a]	
			Rating	Area
		Organic phosphorus compounds		
Creatine phosphate	7.6	23	½,2	2
Creatinine phosphate	7.8	17	0	0
Adenosine triphosphate	7.5	22	1,2	2
Glucose-6-phosphate	7.5	18	½,1	1
Fructose-1,6-diphosphate	7.0	23	½	1
Acetyl phosphate	7.7	24	1	1
Ammonium phytate	7.4	28	1	1
Glycine ethyl ester phosphate	7.0	33	1	3

10 days		Results after 32 days			
P absorbed as % of P applied	P translocated as % of P absorbed	Estimate of leaf damage: Rating	Estimate of leaf damage: Area	P absorbed as % of P applied	P translocated as % of P absorbed
87	97	1	4	-	-
90	100	0	0	-	-
30	95	0	0	32	90
76	100	0	0	-	-
81	100	1	1	-	-
91	99	1	1	-	-
63	84	1	1	-	-
97	98	1,2	6	-	-

Table 15. Absorption and translocation of phosphorus applied in various forms to leaves of soybeans, and damage to the leaves from the applications in Experiment 2

Phosphorus compound	pH	P applied, $\mu g/cm^2$	Results after: Estimate of leaf damage[a]: Rating	Area
Inorganic phosphorus compounds				
Ammonium orthophosphate	7.0	76	1,2	57
Ammonium pyrophosphate	7.0	99	3	57
Ammonium tripolyphosphate	7.9	76	1	37
Ammonium monometaphosphate	7.0	80	3	5
Ammonium tetrametaphosphate	7.0	79	½	7
Ammonium polyphosphate	7.0	79	2,3	8
Potassium metaphosphate	6.6	57-79	0	0
Calcium metaphosphate	4.1	36-60	0	0
Calcium (Si) metaphosphate	4.2	40-69	0	0
Ultraphosphate No. 157	7.0	84	½,1	9
Ultraphosphate No. 165	7.0	78	1	15
Ultraphosphate No. 149	7.0	77	1	11
Urea ammonium orthophosphate	7.8	80	1,2	53
Urea ammonium polyphosphate	7.0	82	3	68
Guanyl urea phosphate	7.2	21	3	100

[a]See Section IV-A5c for a description of the code used to describe the damage to the leaves.

10 days		Results after 32 days			
P absorbed as % of P applied	P trans-located as % of P absorbed	Estimate of leaf damage: Rating	Estimate of leaf damage: Area	P absorbed as % of P applied	P trans-located as % of P absorbed
-	-				
-	-				
-	-				
83	67	1,3	12	-	-
64	69	1	13	67	57
91	51	1,3	24	-	-
11	89	0	0	15	88
10	70	0	0	10	70
11	61	0	0	25	70
80	45	½,1	50	-	-
71	35	0	0	-	-
75	56	1	10	-	-
-	-				
-	-				
-	-				

Table 15. (Continued)

Phosphorus compound	pH	P applied, $\mu g/cm^2$	Results after: Estimate of leaf damage: Rating	Area
			Organic phosphorus compounds	
Creatine phosphate	7.6	23	½	1
Creatinine phosphate	7.8	17	0	0
Adenosine triphosphate	7.5	22	0	0
Glucose-6-phosphate	7.5	18	0	0
Fructose-1,6-diphosphate	7.0	23	0	0
Acetyl phosphate	7.7	24	0	0
Ammonium phytate	7.4	28	½,1	1
Glycine ethyl ester phosphate	7.0	33	3	1

10 days		Results after 32 days			
		Estimate of leaf damage			
P absorbed as % of P applied	P trans-located as % of P absorbed	Rating	Area	P absorbed as % of P applied	P trans-located as % of P absorbed
81	87	1	20	-	-
90	84	1	4	-	-
40	57	0	0	56	80
91	85	0	0	-	-
80	94	0	0	-	-
84	81	1	1	-	-
67	53	1	2	-	-
95	91	3	2	-	-

b. Soybeans Orthophosphate and pyrophosphate caused significantly more damage than the other condensed phosphates. The monometaphosphate and the commercial ammonium polyphosphate were absorbed better than the tetrametaphosphate. The long-chain polyphosphates were absorbed very poorly. The ultraphosphates caused much damage to the leaves or were not well translocated.

The organic phosphates caused little damage, and all except adenosine triphosphate and ammonium phytate were absorbed well.

c. Long-term experiment The condensed phosphates caused an increase of 50 to 100% in the damage to the leaves of both corn and soybeans during the 22-day period following the observations made after 10 days. Ultraphosphate No. 157 caused a larger increase. Glycine ethyl ester phosphate and creatine phosphates caused a 50% increase on corn. Creatinine phosphate caused a tremendous increase in damage on soybeans, which indicates that it is toxic to this crop.

By the 32nd day after application, the absorption of phosphorus from the long-chain condensed phosphates had not increased appreciably over the absorption at the end of the 10th day. A white residue was still clearly visible on the leaves at this time. By the end of the 32nd day, the absorption of adenosine triphosphate was still relatively poor, especially with corn.

D. Phosphorus Screening Experiment No. 3

1. Introduction

It was evident from the results of Experiments 1 and 2 that it should be possible to apply higher concentrations of certain phosphorus compounds than were used previously, especially the condensed phosphates, tripolyphosphate and tetrapolyphosphate and trimetaphosphate and tetrametaphosphate.

For this reason, an experiment was done with concentrations of 3, 6, and 9 micromoles of phosphorus per treatment with all compounds of Experiments 1 and 2 which looked promising. Also included was an investigation of the residual effect over a period of time longer than that employed in Experiment 2.

2. Procedure

Soybeans were planted on September 14, 1971, in number 10 cans in the usual soil mixture, which was thoroughly mixed with 170 ppm of nitrogen, 90 ppm of phosphorus, and 115 ppm of potassium in the form of monobasic potassium phosphate and ammonium nitrate. The soybean variety Hark was the same as used in Experiments 1 and 2. Corn, variety Funk's G-4444, was planted on September 23.

Both crops were planted with nine seeds per pot and were thinned to three plants per pot after emergence. All pots received 5 ml of an iron chelate solution of 2.7 g per liter on October 2. On October 12, the soybeans were placed under lights, which extended the light period to 16 hours per day to keep the plants growing vegetatively. Corn received 250 mg of ammonium nitrate per pot on October 19. The same treatment was also given to both crops on November 12.

The phosphorus treatments were applied in the interval from October 28 to November 2. Two treatments were applied per leaf, one on each side of the main vein, at least 15 cm distant from each other on the youngest mature leaf of the corn plants. With soybeans, two treatments were applied to separate leaflets of the same trifoliate leaf. Three concentrations, 3, 6, and 9 micromoles of P, were applied to each of the three plants per pot. The solutions were applied with a 25-μl automatic micropipet with disposable tips. All solutions contained 0.25% Tween-80. The control treatments (0.25% Tween-80) was regarded as a separate treatment and was applied to two leaf discs per replicate. The long-chain polyphosphates were applied as suspensions in a 0.5% solution of carboxymethyl cellulose to make the suspensions viscous and to reduce application errors. Other phosphates were applied without the carboxymethyl cellulose.

The experiment was laid out with a randomized block design. There were ten replications, two on each of five plants.

Damage to the leaves was visually estimated on the 9th day after the applications were made. On the 10th day, five replicates were sampled for analysis, one on each of the five plants. These samples were used to measure the short-term absorption and translocation.

Estimates of damage to the leaves on the remaining five replicates were made again 40 days after application for corn and 34 days after application for soybeans. The leaves were sampled 41 days after application of the phosphates to corn and 39 days after application of the phosphates to soybeans.

3. Results and discussion

The damage of the phosphates to the leaves in this experiment was in general less than it was for similar concentrations of the same compound in Experiments 1 and 2, but the level of phosphorus absorption was generally lower. The temperatures at the time of application during this experiment were lower (average 75°F) than those at the time of application in Experiments 1 and 2. Most solutions were also applied during the evening hours, after sunset. The leaf stomata close at night, and this should decrease the initial rate of absorption.

The translocation of most compounds in this experiment and Experiment 2 was higher than in Experiment 1, especially for corn. The plants used in Experiment 1 were older and closer to the reproductive stage than the plants in Experiments 2 and 3 at the time of treatment. A lower phosphorus requirement of the plants in Experiment 3 than in Experiment 1 and 2 is a possible explanation for this observation.

a. Corn Table 16 gives the phosphorus content of leaf washings and leaf discs in the control treatments. Table 17

Table 16. Means of the phosphorus content of the leaf washings and leaf discs from the control treatment in Experiment 3

Time between application of phosphates and sampling of leaves, days	Phosphorus per 1.8 cm^2, µg			
	Corn		Soybeans	
	Washing	Discs	Washing	Discs
10	0.62	9.8	0.77	24.1
41	0.62	7.7	0.95	24.1

gives the estimates of damage of the various phosphates to the leaves as well as the data on absorption and translocation of the applied phosphates.

Ammonium tripolyphosphate could be applied at 248 µg P/cm^2 without causing excessive damage. The relative increase in damage to the leaves by ammonium tripolyphosphate between the first sampling and the second was the least of all the condensed phosphates, being only 25%. Of the phosphorus applied, 80% was absorbed within 10 days; 89% of the absorbed phosphorus was transferred out of the treated area within the same time. Ammonium tetrapolyphosphate performed second best and was a close runner-up to tripolyphosphate.

The metaphosphates could be applied at the same high concentration as the polyphosphates, but they were absorbed more slowly than the polyphosphates. Once absorbed, however, the phosphorus of the metaphosphate was translocated as

Table 17. Absorption and translocation of phosphorus applied in various forms to leaves of corn, and damage to the leaves from the applications in Experiment 3

Phosphorus compound	pH	P applied, µg P/cm²	Results after		
			Estimate of leaf damage[a]		P absorbed as % of P applied
			Rating	Area	
Inorganic phosphorus compounds					
Ammonium orthophosphate	7.0	79	0	0	27
		174	3	½	20
		253	3	5	16
Ammonium pyrophosphate	8.2	91	0	0	60
		188	½,3	10	65
		279	1	1	40
Ammonium tripolyphosphate	7.9	78	0	0	59
		154	3	2	80
		248	2,3	4	80
Ammonium tetrapolyphosphate	7.6	67	0	0	58
		136	3	½	64
		219	1,3	4	64
Ammonium monometaphosphate	7.0	78	0	0	23
		160	½,3	½	26
		249	1,3	2	27
Ammonium tetrametaphosphate	7.0	77	½	5	35
		170	½,1	17	53
		270	½,3	27	55
Ammonium polyphosphate	7.0	74	0	0	61
		150	½,3	6	53
		247	½,3	24	-
Potassium metaphosphate	6.2	53	0	0	4
		90	0	0	10
		185	0	0	10

[a]See Section IV-A5c for the code of ratings of leaf damage.

10 days	Results after 41 days				Increase in leaf damage from 10 to 41 days, %
P trans-located as % of P absorbed	Estimate of leaf damage		P absorbed as % of P applied	P trans-located as % of P absorbed	
	Rating	Area			
89	0	0	30	85	0
91	3	½	25	88	0
89	3	9	24	94	80
92	0	0	77	84	0
89	1,3	13	88	90	30
90	1,3	5	51	90	>200
94	0	0	74	92	0
91	3	2	87	94	0
89	1,3	5	89	96	25
90	0	0	63	89	0
89	0	0	84	92	-100
82	½,2	57	85	90	>200
77	½	2	71	94	>200
93	½,3	10	78	96	>200
87	2	15	67	94	>200
90	0	0	37	90	-100
93	½,3	17	57	95	0
97	1,3	12	53	97	-56
76	0	0	74	79	0
79	1,3	20	68	83	>200
-	1,3	25	-	-	4
90	0	0	11	81	0
90	0	0	10	80	0
90	0	0	13	89	0

Table 17. (Continued)

Phosphorus compound	pH	P applied, μg P/cm^2	Results after: Estimate of leaf damage: Rating	Area	P absorbed as % of P applied
Calcium metaphosphate	3.5	114	0	0	9
		167	0	0	7
		236	0	0	7
Calcium (Si) metaphosphate	3.6	65	0	0	10
		155	0	0	4
		282	0	0	10
Ultraphosphate No. 165	7.0	104	0	0	10
		218	0	0	8
		322	½	½	10
Ultraphosphate No. 149	7.1	74	0	0	34
		154	1	1	39
		226	1,3	2	28
Urea ammonium orthophosphate	7.9	78	1,3	6	82
		158	3	39	-
		257	3	71	-
Urea ammonium polyphosphate	7.0	85	1,3	5	80
		173	2,3	30	-
		271	3	85	-
Guanyl urea phosphate	7.0	59	0	0	14
		123	0	0	19
		180	0	0	28
		<u>Organic phosphorus compounds</u>			
Creatine phosphate	7.0	55	1,3	3	84
		107	1,3	2	59
		177	½,3	3	73
Creatinine phosphate	7.0	58	½,3	7	91
		137	½,3	9	-
		209	1,3	15	-

10 days	Results after 41 days				Increase in leaf damage from 10 to 41 days, %
P translocated as % of P absorbed	Estimate of leaf damage: Rating	Estimate of leaf damage: Area	P absorbed as % of P applied	P translocated as % of P absorbed	
91	0	0	14	92	0
90	0	0	15	83	0
87	0	0	10	90	0
85	0	0	10	61	0
83	0	0	7	65	0
94	0	0	15	70	0
80	½	4	16	48	>200
72	0	0	12	56	0
-	0	0	10	61	-100
93	0	0	48	91	0
90	3	1	46	95	0
88	1,3	3	47	92	50
91	1,2	10	88	95	67
-	1,3	49	-	-	26
-	1,3	84	-	-	18
88	2,3	10	-	-	100
-	1,3	26	-	-	-13
-	3	90	-	-	6
83	0	0	16	82	0
90	0	0	26	87	0
82	0	0	34	92	0
94	½,3	10	92	94	>200
88	½,3	4	66	91	100
90	½,3	19	79	98	>200
86	1,3	5	90	97	-29
-	½,3	19	-	-	111
-	1,3	16	-	-	7

Table 17. (Continued)

Phosphorus compound	pH	P applied, μg P/cm²	Results after: Estimate of leaf damage: Rating	Area	P absorbed as % of P applied
Adenosine triphosphate	7.0	66	3	43	-
		133	3	88	-
		213	3	83	-
Glucose-6-phosphate	7.0	48	0	0	67
		100	0	0	85
		153	0	0	83
Fructose-1,6-diphosphate	6.7	57	1	½	71
		120	½	1	87
		193	½,3	8	88
Acetyl phosphate	6.8	83	1	19	-
		159	2,3	46	-
		248	3	68	-
Ammonium phytate	7.0	54	1,2	39	-
		121	2,3	79	-
		171	2,3	129	-
Glycine ethyl ester phosphate	7.0	28	0	0	84
		57	1,3	4	82
		92	1,3	7	-

10 days: P translocated as % of P absorbed	Results after 41 days: Estimate of leaf damage: Rating	Results after 41 days: Estimate of leaf damage: Area	Results after 41 days: P absorbed as % of P applied	Results after 41 days: P translocated as % of P absorbed	Increase in leaf damage from 10 to 41 days, %
-	2,3	50	-	-	16
-	3	103	-	-	17
-	3	196	-	-	136
80	0	0	78	88	0
87	½	12	86	93	>200
85	½	40	88	76	>200
85	1	2	63	92	>200
86	0	0	67	97	-100
90	½,1	8	85	96	0
-	1,3	16	-	-	-16
-	1,2	29	-	-	-37
-	3	92	-	-	35
-	1	43	-	-	13
-	2,3	93	-	-	18
-	2,3	115	-	-	-11
83	½	2	87	87	>200
87	0	0	93	95	-100
-	1,3	9	97	97	29

readily as that of the polyphosphates. The same is true for all the phosphorus compounds.

The long-chain polyphosphates proved once again to be relatively inert. Their absorption was poor. The urea condensed phosphates produced significantly more damage at the high phosphorus concentrations than did the regular condensed phosphates.

The absorption of orthophosphate in this experiment was not as good as it was in Experiment 2. The applications were made at night, and the next morning a crust of residue with flaky structure was visible on the treated area. There was only a small increase in absorption in the three weeks following the analyses made 10 days after application of the phosphates. The increase in damage to the leaves similarly was small. The residue on the leaves did not decrease.

The percentage absorption of the phosphorus added as orthophosphate decreased regularly with an increase in the quantity of phosphorus applied. With pyrophosphate, the percentage absorption of the phosphorus from the heaviest application was considerably less than it was from the two lighter applications. With some of the other phosphates, the percentage absorption increased with the quantity applied. With the remaining phosphates, the results were irregular, the percentage absorption neither greatly increasing nor greatly decreasing with an increase in the quantity applied.

A persistent white residue on the surface of the treated area of the leaves was noted throughout the experiment with pyrophosphate, commercial polyphosphate, and the ultraphosphates. Among the organic phosphates, guanyl urea phosphate and, to a lesser extent, creatine phosphate also left a white residue on the surface of the treated area of the leaves that persisted throughout the experiment.

The organic phosphorus compounds caused either considerable damage to the leaves or a considerable increase in damage between 10 and 41 days after application, or the absorption was poor. Because of these unfavorable results, no further work was done with the organic phosphorus compounds.

b. <u>Soybeans</u> The data on absorption, translocation, and damage to the leaves of soybeans are given in Table 18. Soybeans were more susceptible to damage than corn and tolerated additions of only 2/3 to 3/4 as much phosphorus as did corn. Tetrapolyphosphate appeared to be the best phosphate in this experiment. The translocation of the absorbed phosphorus, however, was rather low.

Orthophosphate was applied during the daytime, and the absorption was much higher than with corn. The damage to the leaves of the soybeans was also much greater than the damage to the leaves of corn. Just as with corn, there was a decrease in percentage absorption with an increase in quantity of phosphorus applied.

The absorption of the metaphosphates was significantly lower than the absorption of the tri- and tetrapolyphosphates.

Table 18. Absorption and translocation of phosphorus applied in various forms to leaves of soybeans, and damage to the leaves from the applications in Experiment 3

Phosphorus compound	pH	P applied, µg P/cm^2	Results after 10: Estimate of leaf damage[a] Rating	Area	P absorbed as % of applied
Inorganic phosphorus compounds					
Ammonium orthophosphate	7.0	79	1,3	10	63
		174	2	36	42
		253	2,3	34	25
Ammonium tetrapolyphosphate	7.6	67	½	3	60
		136	1,2,3	7	-
		219	2,3	59	-
Ammonium monometaphosphate	7.0	78	3	22	36
		160	3	49	-
		249	3	59	-
Ammonium tetrametaphosphate	7.0	77	2,3	8	25
		170	2,3	25	-
		270	1,2,3	39	-
Ammonium polyphosphate	7.0	74	½,3	9	82
		150	2,3	61	-
		247	2,3	82	-
Potassium metaphosphate	6.2	53	0	0	10
		90	0	0	10
		185	0	0	10
Calcium metaphosphate	3.5	114	0	0	15
		167	0	0	13
		236	0	0	13
Calsium (Si) metaphosphate	3.6	65	0	0	14
		155	0	0	8
		282	0	0	5

[a]See Section IV-A5c for the code of ratings of leaf damage.

days	Results after 39 days				Decrease in leaf damage from 10 to 39 days, %
P trans-located as % of P absorbed	Estimate of leaf damage		P absorbed as % of applied	P trans-located as % of P absorbed	
	Rating	Area			
75	1,3	15	69	61	50
66	2,3	44	-	-	22
72	3	65	39	90	90
29	0	0	75	39	-100
-	1,2,3	7	-	-	0
-	2,3	62	-	-	5
57	3	29	26	-	32
-	3	45	-	-	-8
-	3	60	-	-	2
61	2,3	14	41	76	75
-	2,3	27	-	-	8
-	2,3	23	-	-	-41
14	½,3	16	85	26	78
-	2,3	59	-	-	-3
-	2,3	78	-	-	-5
-	0	0	8	-	0
-	0	0	10	-	0
-	0	0	8	38	0
49	0	0	18	70	0
44	0	0	21	70	0
41	0	0	20	70	0
33	0	0	18	24	0
40	0	0	20	40	0
40	0	0	20	40	0

Table 18. (Continued)

Phosphorus compound	pH	P applied, $\mu g\ P/cm^2$	Results after 10		
			Estimate of leaf damage		P absorbed as % of applied
			Rating	Area	
Ultraphosphate No. 165	7.0	104	0	0	37
		218	½,3	7	29
		322	½,2,3	21	20
Ultraphosphate No. 149	7.1	74	1,3	23	-
		154	2,3	62	-
		226	3	64	-
Organic phosphorus compounds					
Creatine phosphate	7.0	35	1	34	-
		107	2	48	-
		177	2,3	80	-
Creatinine phosphate	7.0	58	1,2	36	-
		137	2,3	56	-
		209	3	71	-
Adenosine triphosphate	7.0	66	½,3	23	14
		133	1,2,3	31	-
		213	2,3	52	-
Glucose-6-phosphate	7.0	48	1,3	½	59
		100	1,2	15	-
		153	1,2	28	-
Fructose-1,6 diphosphate	6.7	57	1	1	52
		120	1,2	15	-
		193	1,2	56	-
Acetyl phosphate	6.8	83	1,2	69	-
		159	2,3	142	-
		248	2,3	175	-
Ammonium phylate	7.0	54	0	0	59
		121	1,2	31	-
		171	1,2	46	-
Glycine ethyl ester phosphate	7.0	28	½,1	2	88
		57	1,2	36	-
		92	2,3	31	-

days	Results after 39 days				Decrease in leaf damage from 10 to 39 days, %
P trans-located as % of P absorbed	Estimate of leaf damage		P absorbed as % of P applied	P trans-located as % of P absorbed	
	Rating	Area			
25	0	0	40	30	0
15	1,3	14	30	30	100
18	1,3	42	20	30	100
-	½,3	21	-	-	-9
-	2,3	66	-	-	6
-	3	62	-	-	-3
-	1	34	-	-	0
-	1,2,3	52	-	-	8
-	2,3	84	-	-	5
-	1,2	56	-	-	56
-	1,2,3	81	-	-	45
-	1,3	83	-	-	17
20	½,3	18	17	43	-22
-	1,2,3	16	-	-	48
-	2,3	41	-	-	-21
21	1,3	½	58	44	0
-	1,3	16	51	66	7
-	1,2	28	-	-	0
20	1	1	49	46	0
-	1,2	17	-	-	13
-	1,2	54	-	-	-4
-	1,2,3	68	-	-	-1
-	1,2,3	131	-	-	-8
-	1,2,3	172	-	-	-2
28	0	0	85	67	0
-	½,2	27	-	-	-13
-	1,2,3	30	-	-	-35
6	0	0	90	52	-100
-	1,2,3	40	-	-	11
-	2,3	39	-	-	26

Ultraphosphate No. 165 had an even lower absorption.

Some of the organic phosphates resulted in considerable damage to the leaves when applied at the highest concentration. The percentage absorption of most was moderate or low, and in no case was the translocation of the absorbed phosphorus high.

E. Phosphorus Screening Experiment No. 4

1. Introduction

When the results of Experiments 1, 2 and 3 were compared, it appeared that environmental factors during application of the compounds, and perhaps also during the time following the application, have a considerable effect on the damage to the leaves and the absorption of the phosphorus. Thus it was decided to apply the most promising compounds once more under environmental conditions as homogeneous as feasible to be able to make valid comparisons among the various phosphates. To reduce possible effects due to light intensity, temperature, humidity, plant stress, and perhaps other factors, it was decided to make all the applications within a short time interval and under conditions as nearly standard as feasible without use of growth chambers. Another objective of the experiment was to obtain information on the rate of absorption immediately after application of the solutions to the leaves.

It was noticed in Experiment 3 that some of the treated areas on the leaves of the control corn plants and some others had small yellow-brown spots inside the treated area. When these were observed under a hand lens, it became apparent that they were located around the leaf hairs. Accordingly, it was decided to lower the concentration of Tween-80 because this was considered the most likely cause.

2. Procedure

Hark soybeans were planted in the usual soil mixture with 200 ppm of nitrogen, 50 ppm of phosphorus, and 100 ppm of potassium mixed through it on July 3, 1972. The nutrients were supplied as ammonium nitrate, monobasic potassium phosphate and potassium nitrate. Corn, of variety Funk's G-4444, was planted on August 4. Both plant types were grown with two plants per No. 10 can.

Additions of 25-microliter volumes of the various phosphate solutions were made to the corn plants on September 4 with an automotic pipet. The soybeans received their treatments on September 12. All solutions contained 0.1% Tween-80. All applications were made in the greenhouse laboratory room under artificial light after the plants had been kept there for at least 4 hours.

The experiment was arranged according to a randomized block design with eight blocks and sixteen replications. Two cultures of the controls were included per replicate.

Half of the replicates were sampled 24 hours after application of the phosphorus solutions. Estimates of damage to the leaves and a second sampling were made after 10 days, according to procedures described previously.

3. <u>Results and discussion</u>

a. <u>Observations after 24 hours</u> The results obtained with the control treatment are given in Table 19, and those with the phosphorus treatments are given in Table 20. A high percentage of the phosphorus of orthophosphate was absorbed by leaves of both crops. Most of the phosphorus absorbed from orthophosphate was translocated out of the treated areas of the corn leaves during the first 24 hours after application, but only a little of the phosphorus absorbed by soybean leaves was translocated. The high rate of absorption of orthophosphate may be responsible in part for its toxicity, especially to soybeans, where the translocation is relatively slow. The phosphorus concentration may reach toxic levels in the inter-cellular solution or it may cause damage indirectly, as for example through drastic changes in the pH of the cellular solution. The rate of incorporation of the ammonium into amino acids and protein would probably exceed the rate of in-corporation of the phosphorus into organic phosphorus compounds. This matter will be explored further in Section V. The rate of hydrolysis of pyrophosphate is very low, 46 days for $t_{\frac{1}{2}}$ at a pH value of 7.0 according to Griffith and Buxton (1967), which may explain in part the relatively low values for ab-sorption and translocation of pyrophosphate in the 24-hour period.

Table 19. Means of the phosphorus content of the leaf washings and leaf discs from the control treatment in Experiment 4

Time between application of phosphorus and sampling of leaves, days	Phosphorus per 1.8 cm^2			
	Corn		Soybeans	
	Washings	Discs	Washings	Discs
1	0.67	12.7	1.15	15.7
10	1.16	11.1	2.02	12.4

b. <u>Observations after 10 days</u> Tripolyphosphate proved to be the best compound for application to corn. Tetrapolyphosphate was best for soybeans. The tri- and tetrametaphosphates caused less damage than the polyphosphates, but they were absorbed more slowly. Soybeans also translocated the metaphosphates rather slowly. The extent of visual damage to the leaves of corn from application of tetrapolyphosphates and trimetaphosphates increased considerably from the 10th to the 16th day following application.

Na-Churs product, included in this experiment, had not been tried before. It is a commercial foliar spray product with the phosphorus in the ortho form according to the manufacturers. The 10-day absorption and translocation data for this product were the same as for orthophosphate. Na-Churs product caused more damage than regular orthophosphate of similar phosphorus concentrations, however, an observation

Table 20. Absorption and translocation of phosphorus applied in various forms to leaves of corn and soybeans, and damage to the leaves from the applications in Experiment 4

Phosphorus compound	pH	P applied, µg P/cm^2	Results after 1 day: P absorbed as % of P applied	P translocated as % of P absorbed
		Corn		
Ammonium orthophosphate	7.0	151	78	76
Ammonium pyrophosphate	7.1	204	16	13
Ammonium tripolyphosphate	7.0	188	20	55
Ammonium tetrapolyphosphate	7.0	251	45	54
Ammonium trimetaphosphate	7.6	210	<5	<50
Ammonium tetrametaphosphate	7.0	193	3	46
Na-Churs product	7.0	115	-	-
		Soybeans		
Ammonium orthophosphate	7.0	25	83	<5
Ammonium pyrophosphate	7.1	69	30	21
Ammonium tripolyphosphate	7.0	63	27	26
Ammonium tetrapolyphosphate	7.0	88	30	34
Ammonium trimetaphosphate	8.0	62	3	<20
Ammonium tetrametaphosphate	7.0	67	3	<20
Na-Churs product	7.0	28	-	-

[a]See Section IV-A5c for the code of ratings of leaf damage.

Results after 10 days				Estimates of leaf damage after 16 days[a]	
Estimates of leaf damage[a]		P absorbed as % of P applied	P translocated as % of P absorbed		
Rating	Area			Rating	Area
1	3	96	89	1	4
½,1	49	46	72	½,1	64
1,3	4	67	86	2,3	4
2	75	88	83	2,3	103
½,1	23	53	86	½,1	53
½	10	32	89	½	12
1	10	89	87	-	-
1	2	88	61		
1	13	79	61		
2,3	6	73	46		
½,2	6	84	54		
2	1	24	52		
0	0	6	25		
1,3	11	86	56		

that can probably be accounted for by the significant amounts of potassium, urea, and ammonium nitrate present in the solution.

F. Phosphorus Screening Experiment No. 5

1. Introduction

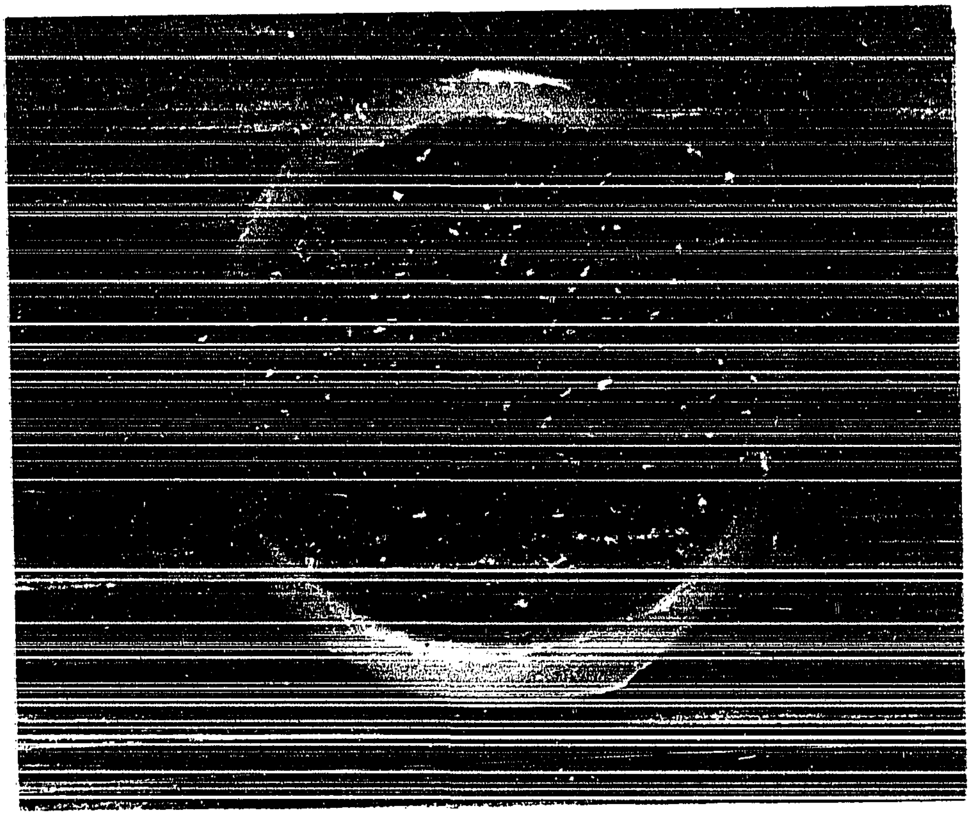
This was a preliminary experiment with three of the four phosphorus-nitrogen compounds obtained from TVA. The purpose was to obtain information on the maximum quantities that could be applied.

2. Procedure

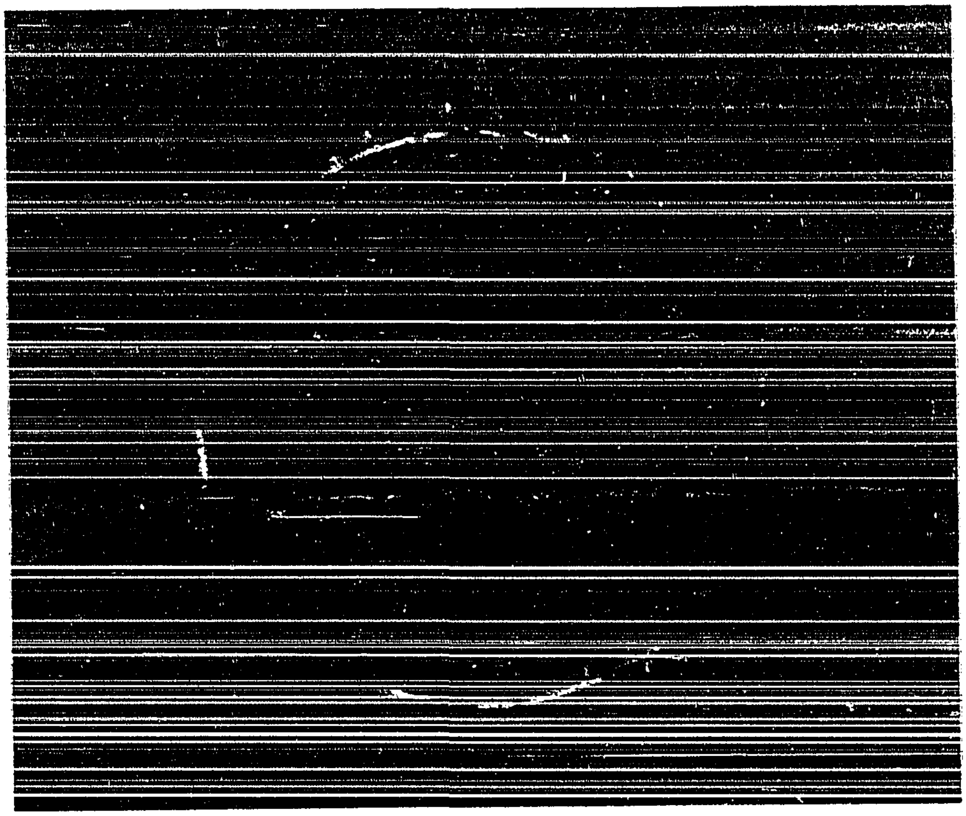
Quantities of 6 and 12 micromoles of phosphorus in 25-microliter volumes of solution containing 0.1% Tween-80 were applied in nine replications to the youngest mature leaves of 2-month-old soybean plants on April 12, 1973. After the phosphates were applied, visual observations were made daily at first and, later, weekly.

3. Results and discussion

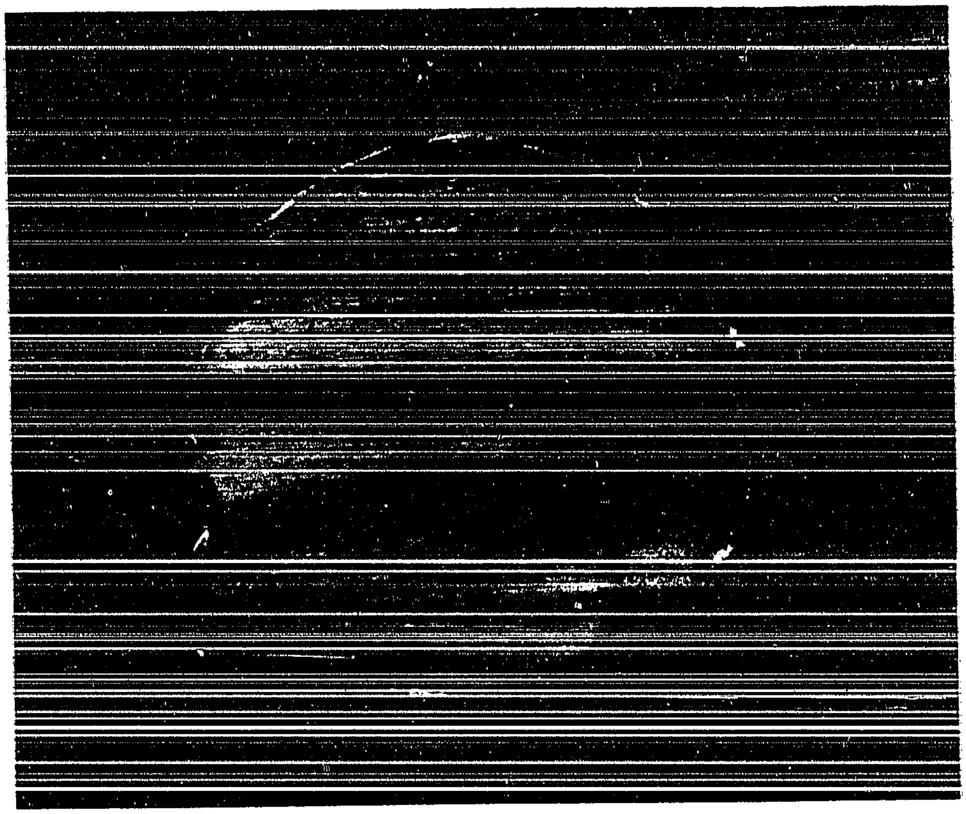
Daily observations during the first week showed that all three compounds initially left dry, crystalline residues on the leaves. Phosphoryl triamide changed to a liquid within 4 to 8 days. The glistening residue of liquid slowly disappeared almost completely during the next 3 weeks. Phosphonitrilic hexaamide behaved similarly, but at a lower rate. (See Photographs 1 and 2 and the results obtained with a lower



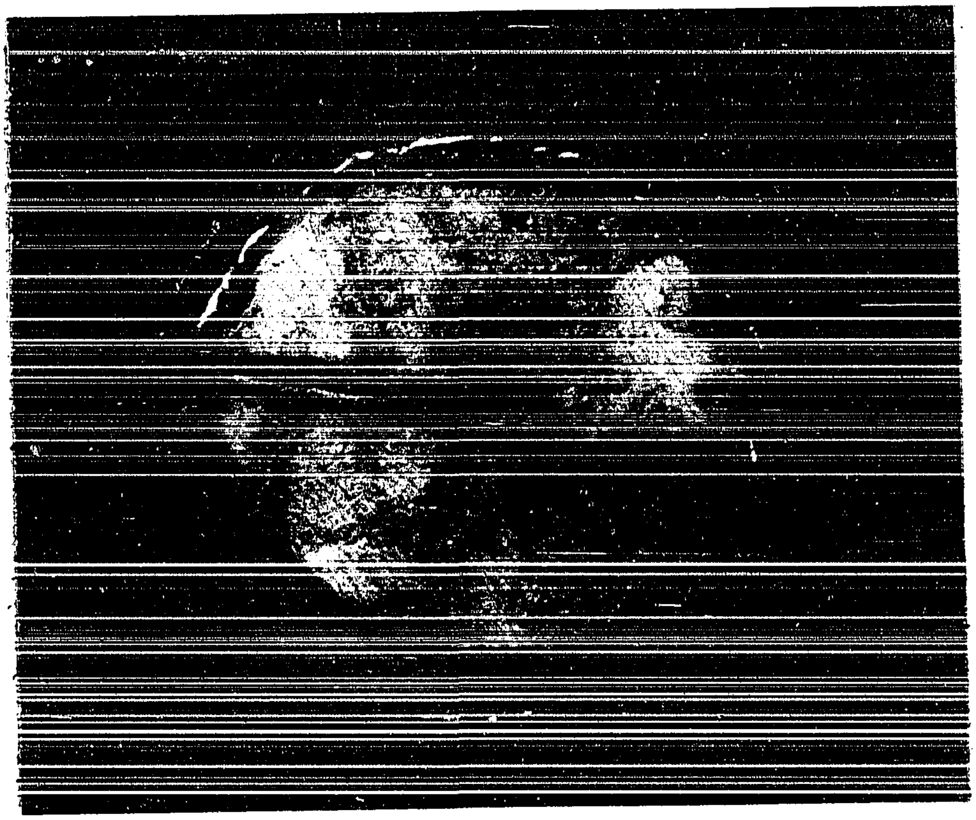
Photograph 1. Appearance of the surface of a corn leaf 1 day after application of 25 µl of a solution containing 12 µmol of phosphorus in the form of phosphonitrilic hexaamide. Note the crystallized residue. The treated portion includes an area of 1.13 cm^2



Photograph 2. Appearance of the surface of a corn leaf 5 days after application of 25 µl of a solution containing µmol of phosphorus in the form of phosphonitrilic hexaamide. The crystallized residue shown in Photograph 1 has changed to a glistening liquid, which gradually disappeared during a period of about 3 weeks. The treated portion includes an area of 1.13 cm^2



Photograph 3. Appearance of the surface of a corn leaf 10 days after application of 25 μl of a solution containing 9 μmol of phosphorus in the form of neutral ammonium orthophosphate. The treated portion includes an area of 1.13 cm^2



Photograph 4. Appearance of the surface of a soybean leaf 10 days after application of 25 µl of a solution containing 6 µmol of phosphorus in the form of neutral ammonium orthophosphate. The treated portion includes an area of 1.13 cm^2

concentration of ammonium orthophosphate under comparable conditions shown in Photographs 3 and 4--these four photographs were made from plants grown at another time.) Ammonium tetrametaphosphimate remained in a flake-like residue on the leaf surface throughout the experiment.

Table 21 gives the quantities of phosphorus applied and the mean estimates of damage to the leaves derived from observations made on the nine replications after 19 and 37 days. Ammonium tetrametaphosphimate caused no observable damage, but the heavy residue remaining at the end of the experiment gave no reason to think that much absorption had occurred. Phosphoryl triamide and phosphonitrilic hexaamide caused about the same amount of damage at 364 μg of P/cm^2, but phosphoryl triamide seemed to have the advantage of being solubilized and absorbed faster than phosphonitrilic hexaamide.

G. Phosphorus Screening Experiment No. 6

1. Introduction

This experiment was done to obtain a quantitative evaluation of the phosphorus-nitrogen compounds that had been supplied by Dr. Z. T. Wakefield of the Tennessee Valley Authority. Orthophosphate was included as a standard source. Certain condensed phosphates were included to make possible a comparison between the new compounds and the best of the condensed phosphates. Also included in this experiment was urea to permit comparison of the amounts of phosphorus and nitrogen that

Table 21. Estimates of damage resulting from application of three phosphorus-nitrogen compounds to leaves of soybeans in Experiment 5

Phosphorus compound	P applied, μg P/cm²	Estimates of damage 19 days after application[a]		Estimates of damage 37 days after application[a]	
		Rating	Area	Rating	Area
Phosphoryl triamide	182	1,3	54	1,3	45
	363	1,3	55	1,3	51
Phosphonitrilic hexaamide	182	1	22	1	26
	364	1,2	49	1,2	68
Ammonium tetra-metaphosphimate	145	0	0	0	0
	289	0	0	0	0

[a]See Section IV-A5c for the code of ratings of leaf damage.

could be applied without unacceptable damage.

2. Procedure

Soybeans were planted on March 29, 1973, in number 10 cans in a soil-sand-peat mixture fertilized with 200 ppm of nitrogen and 160 ppm of potassium in the form of ammonium nitrate and potassium nitrate. Corn was planted on April 6, in a similar soil mixture, except that 20 ppm of phosphorus was added as monobasic potassium phosphate.

Freshly prepared solutions of the various compounds were applied on May 3 through May 6 according to methods described previously. All solutions contained 0.1% Tween-80. The applications were made in the greenhouse laboratory room under artificial light after the plants had been there for at least 2 hours.

There were two applications per corn plant and one to each of the three individual leaflets of a single trifoliate leaf of a soybean plant. The treatments were applied in a randomized-block design with eight replicates. There were two control treatments in each block. Three volumes of each solution were added to empty bottles for subsequent analysis to determine the exact quantities applied. Leaf sampling was done according to methods described earlier, except that the shaking time of the leaf discs in the washing solution was prolonged to 10 minutes.

3. Results and discussion

Table 22 gives the phosphorus content of the leaf discs and washings from the control treatments. These values were used to correct the phosphorus analyses made on the treated leaf discs. Values for the various treatments are given in Tables 23 and 24.

The relatively low absorption of the condensed phosphates in comparison with earlier experiments, especially for corn, may be a consequence of the low humidity, which was 65% at the time of application. The low initial uptake is most likely responsible for the low final uptake, measured after 10 days. The low humidity probably did not influence the phosphorus-nitrogen compounds as much as the condensed phosphates, because

Table 22. Means of phosphorus content of the leaf washings and leaf discs from the control treatment in Experiment 6

Time between application of phosphates and sampling of leaves, days	Phosphorus per 1.8 cm^2, μg			
	Corn		Soybeans	
	Washings	Discs	Washings	Discs
10	0.66	7.44	0.75	16.38
22	1.08	5.73	1.20	21.54

of the property of the phosphorus-nitrogen compounds of changing to a liquid in a few days.

The damage caused to the leaves was also relatively low in comparison with other experiments. This observation confirms the earlier observation that the damage seemed related to the rate of absorption, in particular the rate of absorption in the first hours after application of the phosphorus compound.

The metaphosphates caused less damage and were, as in earlier experiments, absorbed at a lower rate than the polyphosphates. Tripolyphosphate and tetrapolyphosphate performed about equally well.

Phosphoryl triamide appeared to perform at least as well as tripolyphosphate on both crops. Phosphonitrilic hexaamide caused somewhat more damage than phosphoryl triamide on corn, but it could be applied in a greater quantity than phosphoryl

Table 23. Absorption and translocation of phosphorus applied in various forms to leaves of corn, and damage to the leaves from application of the phosphorus compounds and urea in Experiment 6

Compound	pH	Element and application	Estimate of leaf damage[a] Rating	Area	Results after 10 P absorbed as % of P applied
					Condensed
		$\mu g\ P/cm^2$			
Ammonium orthophosphate	7.0	175 367	1 2	1 31	20
Ammonium tripolyphosphate	8.4	168 342	2,3 3	7 22	27
Ammonium tetrapolyphosphate	7.8	188 422	½ ½	6 10	21
Ammonium trimetaphosphate	6.5	169 338	0 1	0 10	14
Ammonium tetrametaphosphate	7.0	164 329	0 2	0 2	11
Ultraphosphate No. 157	7.0	166 367	3 3	16 33	
Ultraphosphate No. 149	7.0	171 333	0 3	0 1	17
					Phosphorus-nitrogen
Phosphoryl triamide	7.1	161 325	½ 1,2	4 12	41
Phosphonitrilic hexaamide	9.9	170 340	2 2	6 16	38

[a]See Section IV-A5c for the code of ratings of leaf damage.

days	Results after 22 days				Increase in leaf damage from 10 to 22 days, %
P trans- located as % of P absorbed	Estimate of leaf damage[a] Rating	Area	P absorbed as % of P applied	P trans- located as % of P absorbed	
phosphates					
94	1	1	51	97	0
	2	32	51	99	3
94	2,3	7	40	96	0
	3	23	39	98	5
92	½	6	34	93	0
	½	10	36	96	0
95	0	0	38	97	0
	1	12	29	99	20
93	0	0	20	97	0
	2	2	22	99	0
	3	17			6
	3	39			18
95	1	2	19	93	>200
	3	1	24	95	0
compounds					
94	1	3	45	100	-25
	1,2	21			75
94	2	10	49	99	67
	½,2	26	46	96	60

Table 23. (Continued)

Compound	pH	Element and application	Results after 10: Estimate of leaf damage[a] Rating	Area	P absorbed as % of P applied
Ammonium trimetaphosphimate	7.6	88	0	0	
		183	1,2	3	30
		364	½,2	21	
Ammonium tetra-metaphosphimate	6.9	117	0	0	4
		233	0	0	
		Urea $\mu g\ N/cm^2$			
Urea		42	0	0	
		84	0	0	
		126	0	0	
		140	0	0	
		154	0	0	
		168	3	4	
		252	3	4	
		336	3	5	

days	Results after 22 days				Increase in leaf damage from 10 to 22 days, %
P trans- located as % of P absorbed	Estimate of leaf damage[a]		P absorbed as % of P applied	P trans- located as % of P absorbed	
	Rating	Area			
93	0	0	26	88	0
	1,2	4	39	94	33
	2,3	24			14
64	0	0	13	93	0
	0	0	28	96	0
	0	0			0
	0	0			0
	0	0			0
	0	0			0
	0	0			0
	3	4			0
	3	4			0
	3	9			80

Table 24. Absorption and translocation of phosphorus applied in various forms to leaves of soybeans, and damage to the leaves from application of the phosphorus compounds and urea in Experiment 6

Compound	pH	Element and application	Estimate of leaf damage[a]		P absorbed as % of P applied
			Results after 10		
			Rating	Area	
					Condensed
		μg P/cm²			
Ammonium orthophosphate	7.0	58	3	3	51
		82	3	27	
		175	3	68	
		367	3	78	
Ammonium tripolyphosphate	8.4	59	2	7	48
		83	3	16	
		168	3	37	
		342	3	54	
Ammonium tetrapolyphosphate	7.8	65	3	12	70
		93	3	31	
		188	3	73	
		422	3	80	
Ammonium trimetaphosphate	6.5	86	0	0	24
		169	0	0	
		338	2	20	
Ammonium tetrametaphosphate	7.0	84	0	0	10
		164	0	0	
		329	3	1	
Ultraphosphate No. 157	7.0	89	3	21	77
		166	3	49	
Ultraphosphate No. 149	7.0	81	3	70	
				Phosphorus-nitrogen	
Phosphoryl triamide	7.1	55	$\frac{1}{2}$,2	3	63
		79	2,3	7	63
		161	3	45	
		325	3	81	

[a]See Section IV-A5c for the code of ratings of leaf damage.

days	Results after 22 days				Increase in leaf damage from 10 to 22 days, %
P trans-located as % of P absorbed	Estimate of leaf damage[a] Rating	Estimate of leaf damage[a] Area	P absorbed as % of P applied	P trans-located as % of P absorbed	
phosphates					
68					
	3	30	83	70	11
	3	72			6
	3	82			5
38					
	3	18	62	45	13
	3	36			-3
	3	58			7
31					
	3	55	85	48	77
	3	73			0
	3	73			-9
86	0	0	25	99	0
	0	0			0
	2	25	18	98	25
65	0	0	5	>70	0
	0	0			0
	3	1	<5	>70	0
32	0	22			5
	3	49			0
	3	68			-3
72					
56	½,3	16	82	86	128
	½,3	50			11
	½,3	88			9

Table 24. (Continued)

			Results after 10		
			Estimate of leaf damage[a]		
Compound	pH	Element and application	Rating	Area	P absorbed as % of P applied
Phosphonitrilic hexaamide	9.9	83	0	0	20
		170	0	0	
		340	½	3	
Ammonium tri-metaphosphimate	7.6	88	1	1	27
		183	1,2	28	
		364	½,2	63	
Ammonium tetra-metaphosphimate	6.9	77	0	0	5
		117	0	0	
		233	3	1	
		Urea			
		μg N/cm^2			
Urea		42	0	0	
		84	0	0	
		98	0	0	
		112	2	3	
		126	2,3	5	
		168	3	22	
		252	3	65	
		336	3	82	

days	Results after 22 days				Increase in leaf damage from 10 to 22 days, %
P trans- located as % of P absorbed	Estimate of leaf damage[a]		P absorbed as % of P applied	P trans- located as % of P absorbed	
	Rating	Area			
69	1	1	44	91	Little
	½	1	32	81	Little
	½,1	17	33	65	>200
54	1	1	34	87	0
	½,3	19			-32
	½,3	61			-3
>50	0	0	14	>60	0
	0	0			0
	3	1	<5	>60	0
	½	7			Little
	½,1	3			Little
	-	-			
	-	-			
	3	6			20
	3	20			-10
	3	68			5
	3	79			-4

triamide. Its absorption, however, was slower than that of phosphoryl triamide.

Trimetaphosphimate showed a severe increase in damage rating from the 10th to the 22nd day after application and it was not absorbed as well as was phosphoryl triamide. Ammonium tetrametaphosphimate did almost no visual damage to the leaves, but it was absorbed very poorly.

Phosphoryl triamide and phosphonitrilic hexaamide behaved as described in Experiment 5. Within a week after application, they were more than 90% transformed to liquids. Ammonium trimetaphosphimate showed a wet appearance on the leaves for about a week and then started to crystallize and turned white. Ammonium tetrametaphosphimate was present as a thick white residue throughout the experiment.

The higher concentrations of the condensed phosphates also showed residues. With the polyphosphates, it took from 1 to 4 days in the greenhouse before some white residue became apparent. The metaphosphates showed a white residue several hours after application. The behavior of the ultraphosphates was similar to that of the polyphosphates.

Comparison of the damage to the leaves among the various compounds tested indicated that urea could be applied without visual damage at a somewhat higher concentration than the well-absorbed phosphorus compounds.

H. Phosphorus Screening Experiment No. 7

1. Introduction

The successful results of Experiment 6 needed confirmation because of the large variations that had been observed among previous experiments.

2. Procedure

The applications were made on May 17 and 18, 1973, to the youngest mature leaves of the same plants used for Experiment 6. The procedures were the same as described previously. The condensed phosphates and all solutions were freshly prepared.

3. Results and discussion

The correction factors, derived from the analyses of the control treatment, are given in Table 25. Tables 26 and 27 give the usual parameters for corn and soybeans, respectively.

Table 25. Means of the phosphorus content of the leaf washings and leaf discs from the control treatment in Experiment 7

Time between application of phosphates and sampling of leaves, days	Phosphorus per 1.8 cm^2, µg			
	Corn		Soybeans	
	Washings	Discs	Washings	Discs
10	1.36	3.53	1.30	23.30

Table 26. Absorption and translocation of phosphorus applied in various forms to leaves of corn, and damage to the leaves from application of the phosphorus compounds and urea in Experiment 7

		Results after 10 days			
	Element and application	Estimates of leaf damage[a]		P absorbed as % of P applied	P translocated as % of P absorbed
Compound	$\mu g\ P/cm^2$	Rating	Area		
		Condensed phosphates			
Ammonium tripolyphosphate	168	3	1	43	77
	252	3	5	51	81
	336	3	42		
Ammonium tetrapolyphosphate	186	½	5	40	68
	280	½	12	31	63
	373	½	62		
Ammonium tetrametaphosphate	321	0	0	9	89
	481	0	0	12	87
		Phosphorus-nitrogen compounds			
Phosphoryl triamide	304	½	66	41	77
	456	½,1	59		
Phosphonitrilic hexaamide	167	½	27	58	80
	250	½,1	48		
	501	2,3	53		
Ammonium trimetaphosphimate	173	½,1	43	49	76
	260	2	88		
		Urea			
	$\mu g\ N/cm^2$				
Urea	168	0	0		
	210	½	2		
	252	½	4		
	294	½,1	4		
	336	½,1	20		

[a]See Section IV-A5c for the code of ratings of leaf damage.

Table 27. Absorption and translocation of phosphorus applied in various forms to leaves of soybeans, and damage to the leaves from application of the various phosphorus compounds in Experiment 7

		Results after 10 days			
		Estimates of leaf damage[a]			
Phosphorus compound	P applied, µg P/cm^2	Rating	Area	P absorbed as % of P applied	P translocated as % of P absorbed
Ammonium orthophosphate	78	$\underline{2}$,3	43	41	63
Ammonium tripolyphosphate	141	0	0	21	<40
Phosphoryl triamide	76 152	3 ½,3	2 23	66	60
Phosphonitrilic hexaamide	334 501	½ $\underline{½}$,1	5 27	33	60
Ammonium trimetaphosphimate	173 260	½,1 $\underline{½}$,1	12 40	34	35

[a]See Section IV-A5c for the code of ratings of leaf damage.

The absorption of all three phosphorus-nitrogen compounds in this experiment was equal to or greater than the absorption in the 6th experiment, perhaps as a consequence of the higher humidity during the first few days after application. The same was true for the condensed phosphates on corn. The percentage translocation was in all cases lower than in the preceding experiment. This observation corresponds with earlier observations in Experiment 1 that lower rates of phosphorus translocation occurred with old plants than with young plants. Observations regarding liquefaction of certain phosphorus-nitrogen compounds and appearance of the residues were the same as those reported in connection with Experiments 5 and 6.

a. Corn Corn showed in general more damage to the leaves in this experiment than in Experiment 6. Phosphoryl triamide and phosphonitrilic hexaamide seemed about equally good, and both seemed slightly better than ammonium tripolyphosphate. Ammonium trimetaphosphimate was absorbed equally as well as the other phosphorus-nitrogen compounds but caused more damage to the leaves. Urea could be applied at about 300-330 $\mu g\ N/cm^2$, which is greater than the amount of phosphorus that could be applied as phosphoryl triamide or phosphonitrilic hexaamide with equivalent damage to the leaves.

b. Soybeans Phosphonitrilic hexaamide was superior to phosphoryl triamide as regards the damage it caused to the leaves, but the percentage absorption of the added phosphorus was greater with phosphoryl triamide than with phosphonitrilic hexaamide. The application of phosphonitrilic hexaamide to soybeans deserves more attention because of the high concentration that can be applied without causing unacceptable leaf damage. Although the percentage absorption was rather low, the total quantity of phosphorus absorbed from phosphonitrilic hexaamide exceeded that absorbed from tri- or tetrapolyphosphate.

I. Summary and General Discussion

The values for absorption and translocation of orthophosphate and some of the more promising phosphates from the various experiments are summarized in Table 28. The condensed phosphates and phosphorus-nitrogen compounds proved to be the most promising compounds for foliar application. Tripolyphosphate was the best condensed phosphate on corn, closely followed by tetrapolyphosphate. These two forms of phosphorus performed about equally well on soybeans. These phosphorus sources could be applied at 2.5 to 3 times the quantity of phosphorus that could be applied as orthophosphate. Soybeans proved to be more sensitive than corn, and could in general tolerate only 2/3 to 3/4 of the quantities of the various compounds that could be applied to corn.

Tri-, and tetrametaphosphates could be applied in even greater quantities (3 to 4 times that of orthophosphate) without causing damage to the leaves, but their rate of absorption was much less than that of the polyphosphates, which makes them less desirable compounds than the polyphosphates. According to Van Wazer (1958), the ring compounds are relatively stable in aqueous solution at neutral pH, and this stability increases with the number of phosphate groups per ring. The relatively low absorption of trimetaphosphate and the even lower absorption of tetrametaphosphate are thus in agreement with Van Wazer's report.

Table 28. Mean values for phosphorus absorption and translocation based on measurements made 10 days after application for the most promising forms of phosphorus employed in the screening experiments in the greenhouse

Form of phosphorus[a]	Corn			Soybeans		
	P absorbed as % of P applied	P translocated as % of P absorbed	No. of experiments	P absorbed as % of P applied	P translocated as % of P absorbed	No. of experiments
Orthophosphate	60-95	92	4	57	67	5
Pyrophosphate	68	84	4	79	59	2
Tripolyphosphate	67	87	6	57	46	4
Tetrapolyphosphate	56	83	4	71	38	3
Trimetaphosphate	52	89	3	43	57	3
Tetrametaphosphate	42	89	6	33	39	6
Phosphoryl triamide	41	86	2	65	63	2
Phosphonitrilic hexaamide	48	87	2	27	65	2
Ammonium triphosphate	40	85	2	31	45	2

[a]The first six were applied as neutral solutions of the ammonium salts.

Neutral solutions of the ammonium salts of orthophosphoric acid, pyrophosphoric acid, and the various metaphosphoric acids tested dried rapidly and, within several hours after application, left on the leaf surface a white dry residue that seemed to cause little further damage. These residues persisted and hence did not seem to be absorbed under the greenhouse conditions employed. Environmental conditions such as humidity, temperature, and light intensity were thought to influence the absorption.

Neutral solutions of ammonium tripolyphosphate and tetrapolyphosphate required up to several days to dry and crystallize after application of the solutions. These compounds were absorbed much less rapidly than the corresponding orthophosphate. The prolonged contact between the leaf and the syrup, however, no doubt permitted absorption to continue at an effective rate for a longer time than would have been the case had the solutions dried quickly. This behavior may be an important factor in the effectiveness of tripolyphosphate and tetrapolyphosphate. The long-chain polyphosphates were applied in suspension form because of their low solubility. They were absorbed very slowly.

The ultraphosphates were either absorbed poorly or translocated poorly. The ultraphosphates are very unstable in water (antibranching rule, Van Wazer, 1958). Their low absorption suggests that their dissolution and primary hydrolysis products are still long-chain and/or ring compounds. The large variation in absorption among experiments was probably due in part to the same causes as for orthophosphate. The higher absorption in Experiment 1 than in the others might be a consequence of the fact that the compounds were dissolved several days before applications.

The urea condensed phosphates were absorbed very well. They caused more damage than did the regular condensed phosphates at high phosphorus concentrations, however. The phosphorus-nitrogen compounds were not as thoroughly tested as some of the condensed phosphates. Their unique property of slow liquefaction of the dried crystals on the leaf surface and their low salt effect as a consequence of their nonionic character (and the occurrence of several phosphorus atoms per molecule of phosphonitrilic hexaamide) may be responsible for the observation that they could be applied in relatively large quantities without causing damage to the leaves.

Neutralization of orthophosphate with organic bases did not prove useful as a technique for increasing the quantity of orthophosphate that could be applied without damage to the leaves. This observation is derived from a review of unpublished work and from results of Experiments 1 and 3.

Some of the organic phosphates tested caused much damage to the leaves when they were added in large quantities. The phosphorus supplied by several of them was not absorbed well.

Under suitable environmental conditions, which are thought to include relatively high humidity and conditions favorable to the presence of open stomates, orthophosphate was absorbed rapidly. The rapid intake of phosphorus is suspected to be an important reason for the damage to the leaves that was observed with applications of no more than 120 to 150 μg of P/cm^2 to corn and 60 to 90 μg P/cm^2 to soybeans. Corn showed a high translocation (76% of the absorbed P) during the first 24 hours. Soybeans translocated less than 5% of the absorbed phosphorus during the first 24 hours after application. The rapid increase in concentration of phosphate in the cell solution might alter the cell pH or produce toxic effects in other ways. Because of the rapid incorporation of the accompanying ammonium ion into organic forms, the cells should become more acid as a result of the residual phosphoric acid.

The phosphorus absorbed from all compounds was translocated by young corn plants to the extent of 80% or more, irrespective of the quantity added. With soybeans, the translocation was much poorer. This observation suggests that the greater sensitivity of soybeans than of corn to foliar applications of phosphorus may be, in part at least, a consequence of relatively slow transport of absorbed phosphorus from the treated areas.

The ratio of the percentage translocation of the phosphorus of a number of the compounds to the phosphorus translocated from orthophosphate was lower with soybeans than with corn. This observation suggests two possibilities. First, soybeans may translocate these forms of phosphorus more slowly than does corn. Second, neither species may transport the compounds readily, and the relatively slower transport in soybeans may be a consequence of slower hydrolysis of the compounds to orthophosphate. At this time, it is not known whether the nonorthophosphates are absorbed as such or whether they are first hydrolyzed to orthophosphate.

Van Wazer (1958) and Griffith and Buxton (1967) gave the following times for hydrolysis of 5% of the P-O-P linkages originally present in a 1% solution at pH 7 and at 20°C: pyrophosphate, 1-2 years; tripolyphosphate, 3 months; tetrapolyphosphate, 1 month; and long-chain polyphosphate, 10-30 years. A 5°C rise in temperature doubles the rate, and the rate increases 1,000 to 10,000 times from a strongly basic to a strongly acid solution.

The rates of absorption measured in the experiments reported here are much higher than the rates of hydrolysis of the various phosphates in water, and so it is almost certain that, if hydrolysis to orthophosphate is necessary for absorption, enzyme activity has played an important role in hastening the hydrolysis. Van Wazer (1958) reported that enzymes can increase the rate of hydrolysis by as much as 100,000 times. Whether the enzymes act outside the leaf or only on the inside is not known. Neither is it known how specific they are with respect to their substrate.

Coic et al. (1965a, 1965b) and Roux (1968) found that plant roots are capable of absorbing pyrophosphate. Z. T.

Wakefield (Division of Chemical Development, Tennessee Valley Authority, Muscle Shoals, Alabama, unpublished data) found that the absorption by oat plants of phosphoryl triamide was faster, and that the absorption of phosphonitrilic hexaamide was slower, than was the absorption of diammonium orthophosphate as a source of phosphorus in solution. Both covalent compounds were absorbed unaltered by plant stems and were hydrolyzed rapidly to orthophosphate in the plant stems, phosphonitrilic hexaamide at a slower rate than phosphoryl triamide.

The evidence just cited suggests that absorption by leaves of unaltered phosphorus compounds of higher molecular weight than orthophosphate is likely and that most transported phosphorus is probably in the orthophosphate form. Another indirect indication that plants can absorb higher condensed phosphates directly is the fact that considerable "damage" rated "1/2" (slight discoloring of the treated area) was observed 10 days after application of the tetrametaphosphate. This slight discoloration disappeared completely after several weeks.

The lower absorption rate of most compounds in Experiment 3 than in other experiments may be related to the fact that Experiment 3 was done in the fall, when plants grow more slowly than in the spring or summer. The relatively slow translocation rates of most compounds in Experiments 1 and 7 is probably related to the greater physiological maturity of these plants and their lower phosphorus requirement.

V. SOME FACTORS INFLUENCING FOLIAR FERTILIZATION WITH PHOSPHORUS

A. Effect of Solution pH, Experiment 8

1. Introduction

At the same time that Experiment 1 was done, two other phosphorus compounds, ammonium pyrophosphate and ammonium tripolyphosphate, were also applied at a lower and a higher pH than 7.0 to determine whether the pH of the solution applied to the leaves affects the concentration that can be applied and the absorption of the phosphorus. The procedures used in this experiment were the same as for Experiment 1.

2. Results and discussion

Table 29 gives the visual estimates of damage to the leaves and the measurements of absorption and translocation made 18 days after application of the two different phosphorus compounds at three different pH values to leaves of corn and soybeans.

Ammonium pyrophosphate caused more damage than ammonium tripolyphosphate. The damage became more severe as the pH decreased from 8.2 to 3.9. With tripolyphosphate, the pH had little influence on the damage to the leaves.

The absorption of the phosphorus supplied by the two compounds was little affected by pH. The translocation of the phosphorus of the 82 μg P/cm^2 application of pyrophosphate at pH 8.2 was lower with both crops than was that of the 28 μg

Table 29. Absorption and translocation of phosphorus applied as solutions of ammonium salts of pyrophosphoric acid and tripolyphosphoric acid at different pH values to leaves of corn and soybeans, and damage to the leaves resulting from application of these solutions in Experiment 8

			Results after 18 days			
			Estimates of leaf damage[a]		P absorbed as % of P applied	P translocated as % of P absorbed
Phosphorus compounds	pH	P applied, $\mu g\ P/cm^2$	Rating	Area		
			Corn			
Ammonium pyrophosphate	3.9	36	1	18	69	90
		115	1,3	50	74	67
	6.9	29	0	0	82	79
		85	1,3	15	87	74
	8.2	29	1	5	75	71
		82	1	10	89	49
Ammonium tripolyphosphate	4.8	28	1	1	83	71
		82	3	10	92	91
	7.1	28	0	0	83	66
		82	1	5	94	68
	8.0	28	0	0	82	78
		82	1	5	91	62
			Soybeans			
Ammonium pyrophosphate	3.9	36	1	1	66	59
		115	3	68	-	-
	6.9	29	0	0	80	57
		85	1,3	50	-	-
	8.2	29	0	0	59	71
		82	1,2	23	67	45

[a]See Section IV-A5c for the code of ratings of leaf damage.

Table 29. (Continued)

Phosphorus compounds	pH	P applied, µg P/cm²	Results after 18 days: Estimates of leaf damage: Rating	Area	P absorbed as % of P applied	P translocated as % of P absorbed
Ammonium tripolyphosphate	4.8	28	0	0	79	63
		82	2,3	38	-	-
	7.1	28	0	0	85	60
		82	1,3	50	95	39
	8.0	28	1	8	83	53
		82	2,3	41	-	-

P/cm^2 application, which suggests that at pH 8.2 the higher concentration of pyrophosphate inhibited the rate of hydrolysis. This observation is at variance with results of the phosphorus screening experiment in which there was no indication of decreased translocation with an increase in concentration at pH 7.0. Whether these observations have broad significance for nonorthophosphate forms of phosphorus in general remains to be determined. Several different mechanisms might conceivably contribute to the behavior observed.

B. Effect of Solution pH, Experiment 9

1. Introduction

The results of the eighth experiment and the possible role of the pH effect seemed to justify another experiment with a wider pH range, sampling times of 24 hours and 10 days after application, and use of the more successful tripolyphosphate compound instead of the pyrophosphate besides orthophosphate, which might be considered a standard source.

This experiment was conducted parallel to Experiment 4 and the same procedures and analyses of the control samples were used.

2. Results and discussion

Table 30 gives the estimates of damage to the leaves after 10 days and the measurements of absorption and translocation made 24 hours and 10 days after application of the phosphates. With both compounds and both crops, there was more damage to the leaves from the acid and basic solutions than from the neutral solutions. With all four combinations of compounds and crops, there was more damage to the leaves at pH 2.0 than at pH 10.0.

Values for absorption and translocation of the phosphorus after 24 hours and 10 days are given in Table 30 and are plotted in Figures 3 through 6. Table 31 gives the F-values of various variables and their statistical significance.

Most of the applied orthophosphate was absorbed by leaves of both crops within the first 24 hours. The absorption did not differ significantly between crops. There was no significant pH effect, although with soybeans there was a consistent upward trend of absorption with pH. After 10 days, there was

Table 30. Absorption and translocation of phosphorus applied as solutions of ammonium salts of orthophosphoric acid and tripolyphosphoric acid at different pH values to leaves of corn and soybeans, and damage to leaves resulting from application of these solutions in Experiment 9

pH of applied solution	Results after 24 hours: P absorbed as % of P applied	Results after 24 hours: P translocated as % of P absorbed	Results after 10 days: Estimates of leaf damage[a]: Rating	Results after 10 days: Estimates of leaf damage[a]: Area	Results after 10 days: P absorbed as % of P applied	Results after 10 days: P translocated as % of P absorbed
151 µg P/cm² as orthophosphate applied to corn						
2.0	92	84	3	28	97	92
4.0	82	73	½,1	13	97	87
5.5	65	67	½,1	8	97	85
7.0	83	73	1	3	97	87
8.5	92	74	½,1	28	96	85
10.0	93	69	½,1	20	97	83
188 µg P/cm² as tripolyphosphate applied to corn						
2.0	84	68	1,2	41	93	85
4.0	43	47	2	27	90	83
5.5	20	43	1,2	7	87	91
7.0	20	57	1,3	4	67	79
8.5	9	66	2,3	3	43	87
10.0	9	75	2,3	14	44	77
26 µg P/cm² as orthophosphate applied to soybeans						
2.0	71	3	1	6	81	80
4.0	80	<1	2	5	87	85
5.5	82	<1	1	4	88	78
7.0	84	3	1	2	88	61
8.5	84	6	1	2	87	83
10.0	85	7	1	4	85	79

[a]See Section IV-A5c for the code of ratings of leaf damage.

Table 30. (Continued)

	Results after 24 hours		Results after 10 days			
			Estimates of leaf damage			
pH of applied solution	P absorbed as % of P applied	P translocated as % of P absorbed	Rating	Area	P absorbed as % of P applied	P translocated as % of P absorbed
$63\ \mu g\ P/cm^2$ as tripolyphosphate applied to soybeans						
2.0	57	23	1,2	20	83	62
4.0	36	<5	2	1	77	49
5.5	29	<5	2,3	7	78	36
7.0	27	17	2,3	6	73	45
8.5	22	7	2	25	69	29
10.0	26	12	2	17	66	28

still no significant effect of pH on the absorption, but the absorption by corn was significantly greater than the absorption by soybeans. The translocation of orthophosphate within the first 24 hours and 10 days after application was similarly little affected by the pH.

In the first 24 hours after application of the phosphate solutions to the leaves, the absorption of phosphorus applied to both corn and soybeans as tripolyphosphate decreased with an increase in pH value of the solutions from 2 to 10. At the end of 10 days, the pH effect had disappeared completely with soybeans, but not with corn.

The translocation of the phosphorus absorbed from tripolyphosphate was greater at both samplings in corn than in

Figure 3. Absorption of phosphorus in 24 hours by leaves of corn and soybeans from solutions of the ammonium salts of orthophosphoric and tripolyphosphoric acids at different pH values applied to the leaves in Experiment 9

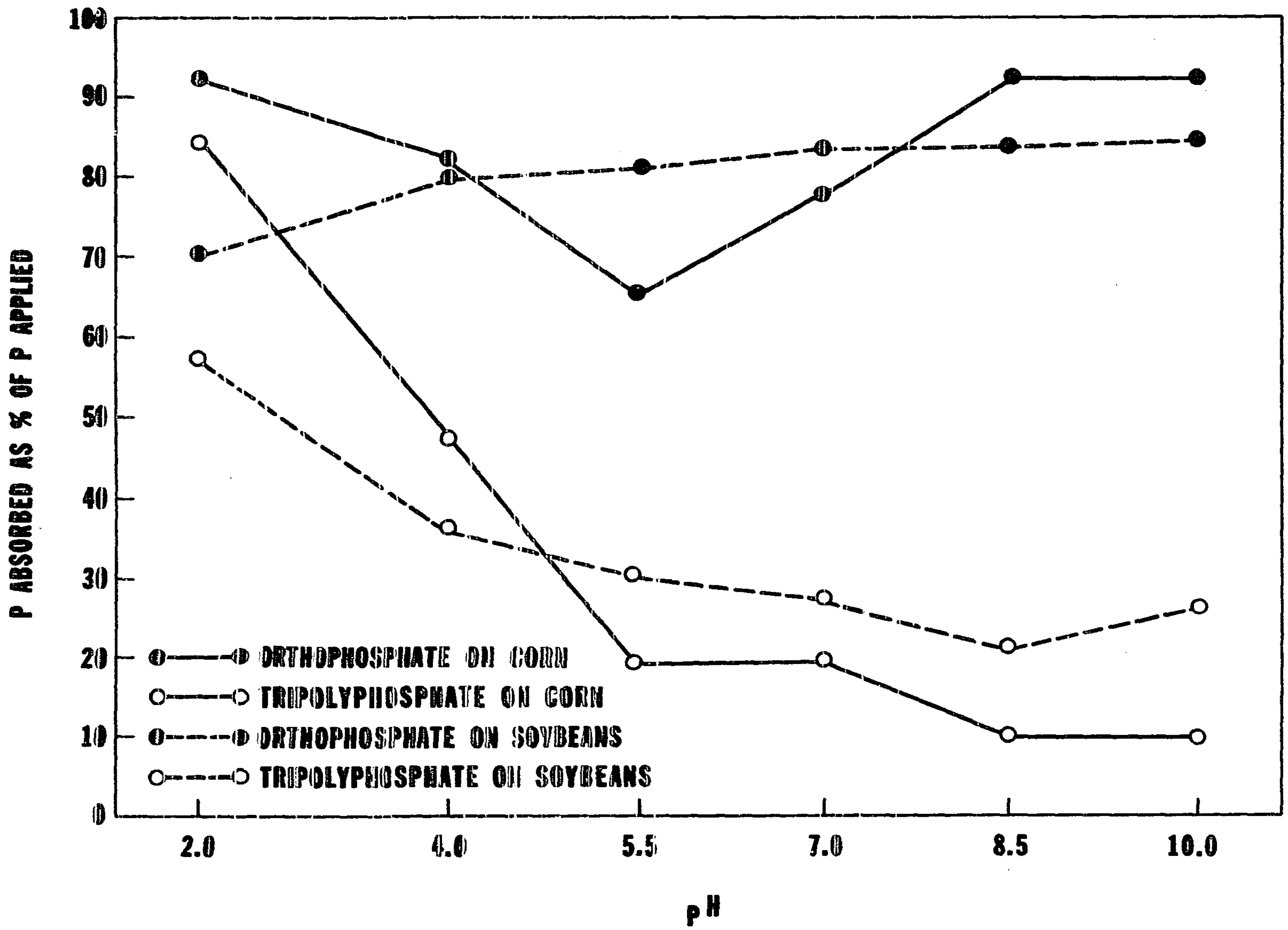

P ABSORBED AS % OF P APPLIED
100
90
80
70
60
50
40
30
20
10
0
2.0
4.0
5.5
7.0
8.5
10.0
pH
ORTHOPHOSPHATE ON CORN
TRIPOLYPHOSPHATE ON CORN
ORTHOPHOSPHATE ON SOYBEANS
TRIPOLYPHOSPHATE ON SOYBEANS

Figure 4. Absorption of phosphorus in 10 days by leaves of corn and soybeans from solutions of the ammonium salts of orthophosphoric and tripolyphosphoric acids at different pH values applied to the leaves in Experiment 9

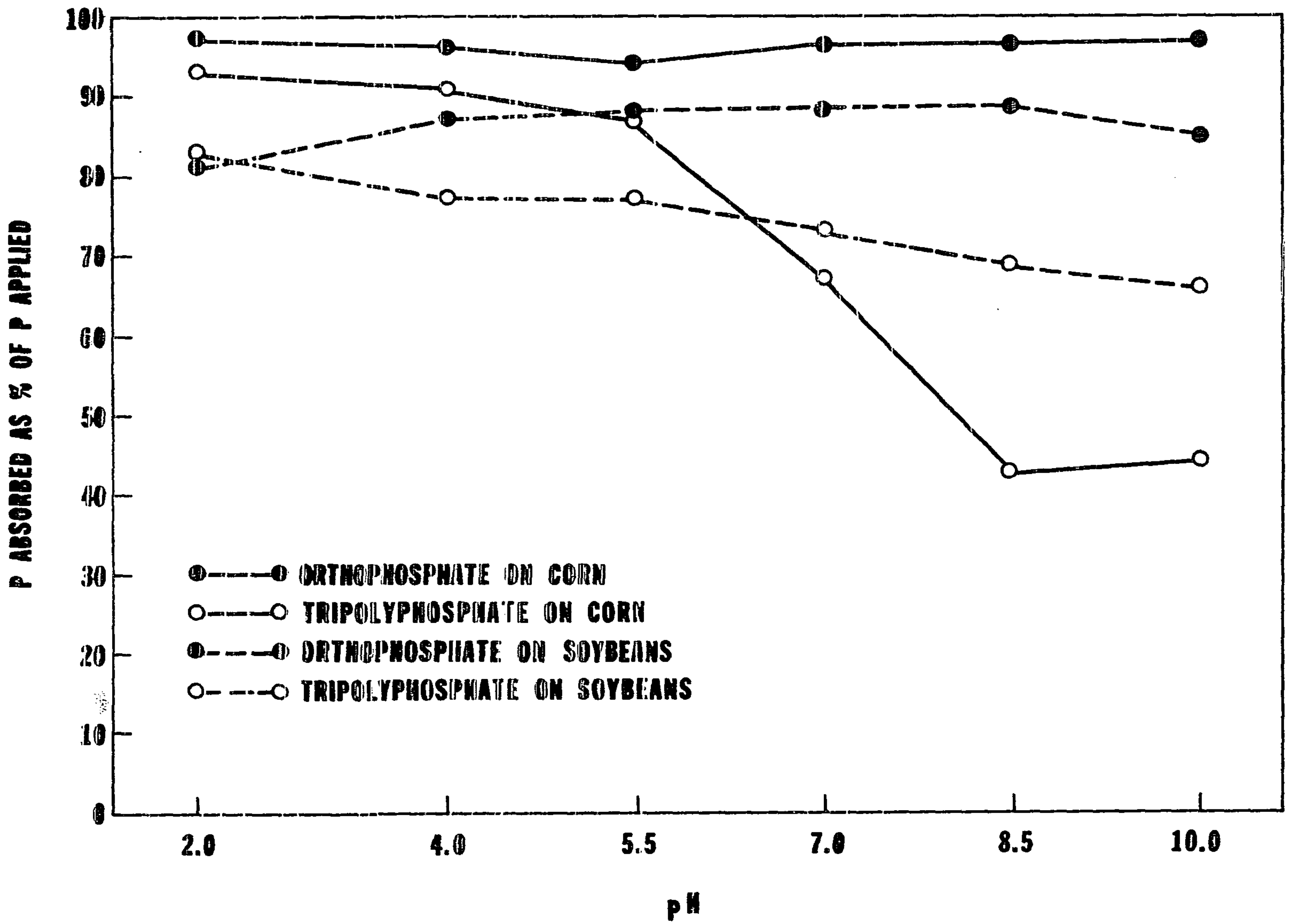

P ABSORBED AS % OF P APPLIED
100
90
80
70
60
50
40
30
20
10
0
ORTHOPHOSPHATE ON CORN
TRIPOLYPHOSPHATE ON CORN
ORTHOPHOSPHATE ON SOYBEANS
TRIPOLYPHOSPHATE ON SOYBEANS
2.0
4.0
5.5
7.0
8.5
10.0
pH

Figure 5. Translocation of foliar-applied phosphorus by leaves of corn and soybeans in the 24-hour period following application of the ammonium salts of orthophosphoric and tripolyphosphoric acids at different pH values in Experiment 9

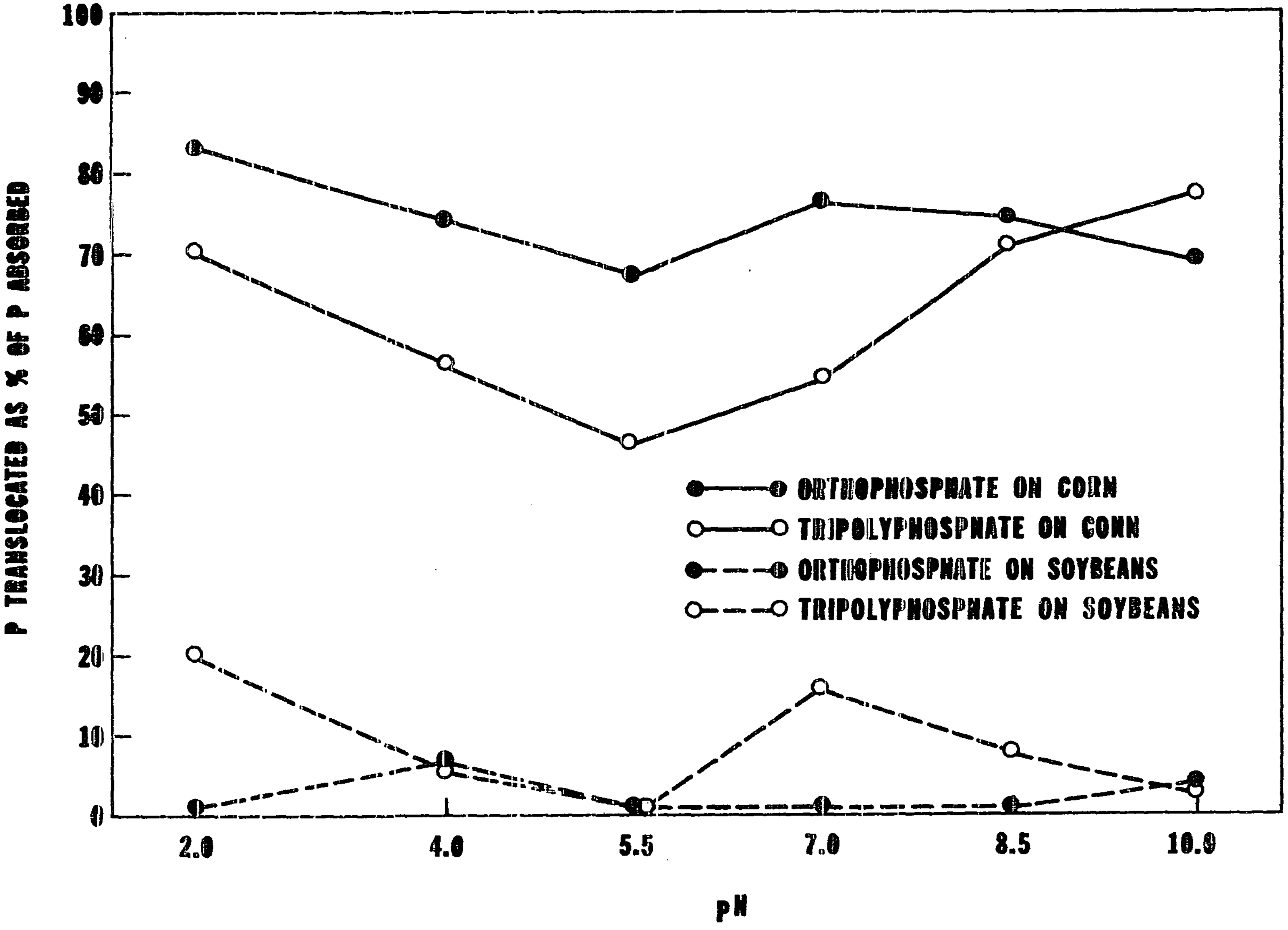

P TRANSLOCATED AS % OF P ABSORBED
100
90
80
70
60
50
40
30
20
10
0
ORTHOPHOSPHATE ON CORN
TRIPOLYPHOSPHATE ON CORN
ORTHOPHOSPHATE ON SOYBEANS
TRIPOLYPHOSPHATE ON SOYBEANS
2.0
4.0
5.5
7.0
8.5
10.0
pH

Figure 6. Translocation of foliar-applied phosphorus by leaves of corn and soybeans in the 10-day period following application of the ammonium salts of orthophosphoric and tripolyphosphoric acids at different pH values in Experiment 9

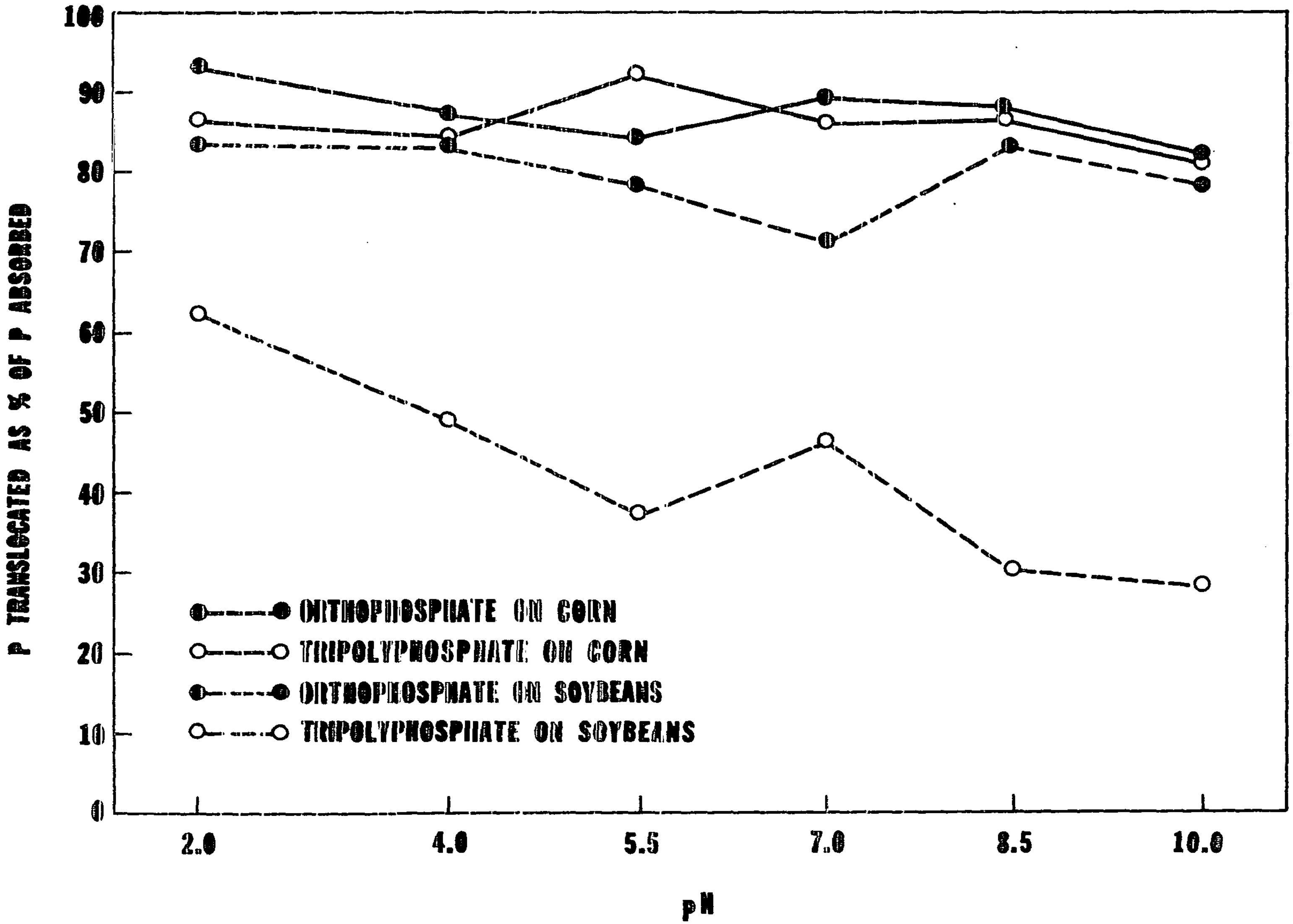

P TRANSLOCATED AS % OF P ABSORBED
100
90
80
70
60
50
40
30
20
10
0
2.0
4.0
5.5
7.0
8.5
10.0
pH
ORTHOPHOSPHATE ON CORN
TRIPOLYPHOSPHATE ON CORN
ORTHOPHOSPHATE ON SOYBEANS
TRIPOLYPHOSPHATE ON SOYBEANS

Table 31. F-values and coefficients of variation associated with various variables in Experiment 9

Variable	F-values for indicated sources of variation			Coefficient of variation
	pH (A)	Crops (B)	A x B	
Absorption of orthophosphate by corn and soybeans after 24 hours	<1	<1	15.45**	7.7
Absorption of orthophosphate by corn and soybeans after 10 days	<1	72.14**	2.82*	3.7
Absorption of orthophosphate by both crops after 24 hours and 10 days	<1	2.63	12.30**	8.3
Absorption of tripolyphosphate by corn and soybeans after 24 hours	6.27*	<1	12.14**	29.9
Absorption of tripolyphosphate by corn and soybeans after 10 days	2.38	<1	15.96**	11.0
Absorption of tripolyphosphate by both crops after 24 hours and 10 days	3.88+	<1	3.95**	46.2
	pH (A)	P treatments (B)	A x B	
Translocation of ortho- and tripolyphosphate by corn after 24 hours	1.71	8.24*	4.79**	16.3
Translocation of ortho- and tripolyphosphate by corn after 10 days	1.69	2.19	3.20**	6.1
Translocation of both compounds by corn after 24 hours and 10 days	3.56**	13.87**	1.05	19.3
Translocation of ortho- and tripolyphosphate by soybeans after 24 hours	1.68	<1	<1	84.1

+,*,**Indicate significance at 10%, 5%, and 1% levels, respectively.

Table 31. (Continued)

Variable	F-values for indicated sources of variation			Coefficient of variation
	pH (A)	P treatments (B)	A x B	
Translocation of ortho- and tripolyphosphate by soybeans after 10 days	<1	31.60**	9.78**	16.7
Translocation of both compounds by soybeans after 24 hours and 10 days	1.10	7.86**	1.70	23.5
Translocation of orthophosphate by both crops and tripolyphosphate by corn after 10 days	3.84**	1.17	1.37	11.2
	pH (A)	Time (B)	A x B	
Absorption of orthophosphate by corn after 24 hours and 10 days	2.56	8.06*	7.28**	7.0
Absorption of orthophosphate by soybeans after 24 hours and 10 days	5.08*	12.94*	2.73*	4.9
Absorption of tripolyphosphate by corn after 24 hours and 10 days	7.27*	25.74**	12.26**	20.8
Absorption of tripolyphosphate by soybeans after 24 hours and 10 days	5.09*	144.48**	4.99**	14.5
Translocation of orthophosphate by corn after 24 hours and 10 days	14.64**	121.68**	1.12	6.5
Translocation of orthophosphate by soybeans after 24 hours and 10 days	3.17	410.33**	2.57*	27.5
Translocation of tripolyphosphate by corn after 24 hours and 10 days	<1	14.54*	6.60**	16.4
Translocation of tripolyphosphate by soybeans after 24 hours and 10 days	3.14**	30.70**	1.17	40.7

soybeans. The translocation in the first 24 hours after application was not affected by the pH of the solution with either crop. In the sampling 10 days after application, however, the translocation decreased with an increase in pH of the solution with soybeans. There may have been an effect of pH in the first 24 hours as well as in the first 10 days, but the translocation in the first 24 hours was so limited in soybeans that errors of measurement were relatively high. The results of the sampling made 10 days after application showed a significantly greater translocation of phosphorus from orthophosphate than from tripolyphosphate in soybeans but not in corn.

C. Effect of Procedural Techniques on the Damage to the Leaves, Experiment 10

1. Introduction

The results described in previous sections indicate that the rate of phosphorus absorption by leaves and the extent of visible damage to the leaves are strongly related.

Woolley (1961) and Linskens et al. (1965) found that the areas around the base of leaf hairs absorb much faster than other areas of the leaf surface and that leaf hairs are easily broken. Part of the procedure used in the screening experiments was to spread the 25-µl volume of solution over the area enclosed by the wax circles. This procedure undoubtedly broke some of the leaf hairs. The experiment described in this section was done to determine whether spreading the phosphorus solution with the glass rod increased the damage to the leaves.

2. Procedure

The youngest mature leaves of 6-week-old corn and soybean plants were sprayed on September 4 in eight replications. The leaves were kept in a horizontal position on a table by some rubber stoppers and were sprayed with a hand-pump sprayer equipped with a fine nozzle until the droplets started to touch each other and run off. One portion of each leaf was treated with a glass rod in the conventional way, as was done in the screening experiments. Several compounds, listed in Table 32, were used as treatments, and all solutions contained 0.1% Tween-80. Other plants were treated with 25-µl volumes of phosphorus solutions inside a paraffin-lanolin ring with surface area of 1.13 cm^2, as was done in the screening experiments. Estimates of damage to the leaves were made 10 days after application of the solutions.

3. Results and discussion

The mean damage estimates over eight replications of three different methods of applying the phosphorus solutions to corn leaves are given in Table 32. Corresponding results with soybeans are given in Table 33.

Spreading the solution over the leaf surface with the fine-polished tip of a glass rod produced some increase in

Table 32. Estimates of damage to leaves of corn plants resulting from three methods of applying various phosphate solutions at different pH values to the leaves

Forms of phosphorus applied as ammonium salts	P in solution applied %	pH	Estimates of damage to leaves[a] 10 days after application of solutions by the methods indicated					
			Sprayed		Sprayed and spread		Spread in rings	
			Rating	Area	Rating	Area	Rating	Area
Orthophosphate	0.7	2.0	2,3	24	2,3	17	3	28
		4.0	1	2	1	4	½,1	13
		5.5	2	4	2	4	½,1	8
		7.0	0	0	0	0	$\overline{1}$	3
		8.5	1,2	7	1,2	8	½,1	28
		10.0	3	69	3	74	½,1	20
Tripolyphosphate	0.8	2.0	2	14	2	14	1,2	41
		4.0	1,$\underline{2}$	4	1,$\underline{2}$	8	2	27
		5.5	½,$\overline{1}$	4	½,$\overline{1}$	2	1,2	7
		7.0	1	1	1	2	1,$\underline{3}$	4
		8.5	1	1	1	1	2,$\underline{\overline{3}}$	3
		10.0	1	3	1	4	2,$\overline{3}$	14
Pyrophosphate	0.9	7.1	1	5	½,1	6	½,1	49
Tetrapolyphosphate	1.1	7.0	2	5	2	14	$\overline{2}$	75
Trimetaphosphate	0.9	7.6	½,1	8	½,1	8	$\underline{½}$,1	23
Tetrametaphosphate	0.9	7.0	½	4	½	2	$\overline{½}$	10
Control (0.1% Tween-80)	0	7.0	0	0	0	0	0	0

[a]See Section IV-A5c for the code of ratings of leaf damage.

Table 33. Estimates of damage to leaves of soybean plants resulting from three methods of applying various phosphate solutions at different pH values to the leaves

Forms of phosphorus applied as ammonium salts	P in solution applied %	pH	Estimates of damage to leaves[a] 10 days after application of solutions by the methods indicated: Sprayed		Sprayed and spread		Spread in rings	
			Rating	Area	Rating	Area	Rating	Area
Orthophosphate	0.4	2.0	2	10	2	15	1,3	92
		4.0	2	5	2	7	1,3	73
		5.5	1	6	1	5	2	67
		7.0	1	5	1,2	4	2	61
		8.5	1	5	1	6	1,2	49
		10.0	2,3	15	2,3	19	2	65
Tripolyphosphate	0.7	2.0	3	3	3	4	3	85
		4.0	3	15	3	10	3	78
		5.5	2,3	8	2,3	6	3	80
		7.0	2,3	8	3	6	3	71
		8.5	3	8	3	11	3	70
		10.0	3	13	3	19	3	83
Pyrophosphate	0.6	7.1	3	8	3	5	3	83
Tetrapolyphosphate	0.7	7.0	1	30	1	34	2	95
Trimetaphosphate	0.7	8.0	0	0	0	0	2	3
Tetrametaphosphate	0.7	7.0	0	0	0	0	0	0
Control (0.1% Tween-80)	0	7.0	0	0	0	0	0	0

[a]See Section IV-A5c for the code of ratings of leaf damage.

damage to the leaves of soybeans from the acid and basic solution of orthophosphate. The spreading action seemingly broke some of the leaf hairs. Corn plants have fewer and different leaf hairs than do soybeans, and no increase in damage to the leaves due to spreading of the phosphorus solutions was observed.

The most remarkable effects of method are found in the much greater damage to the leaves on which the phosphate solutions were applied by a pipet and spread manually in the wax ring than to the leaves that were sprayed with the phosphate solutions. When the experiment was planned, it was thought that the damage done to the leaves when the wax rings were applied could be evaluated by comparing the "ring" treatment with the treatment in which the solutions were sprayed on the leaves and spread without the rings. Although some damage to the leaves no doubt resulted from making the rings, it seems unlikely that the damage from this cause was as great as that implied by the difference in results between the two treatments in question. One other difference between the "ring" and "spray" treatments was that, in the absence of the wax rings, the sprayed leaves would not hold as great a volume of solution per unit area as was applied within the rings. This experimental difficulty could readily be remedied by changing the procedures. Additional work is needed to clarify the matter.

D. Differential Absorption of Tripolyphosphate by Leaves of Corn Plants of Differing Cytoplasms, Experiment 11

1. Introduction

The cytoplasm associated with male sterility in corn, Texas type (Tcms), is differentially sensitive to infection by the fungus, *Helminthosporium maydis* Nisikado and Miyake, race T (Hooker et al., 1970; Turner and Martinson, 1972). The disease selectively attacks inbreds and hybrids of corn with Tcms cytoplasm, but plants with normal (N) cytoplasm are relatively resistant.

Aside from the male sterile phenotype, major differences distinguish Tcms and N cytoplasm in the presence of the pathotoxin of *H. maydis*. Tcms shows several effects not observed with N. After exposure of Tcms to the pathotoxin, several investigators have reported leaf chlorosis and necrosis (Turner and Martinson, 1972; Gracen et al., 1971), inhibition of seedling root elongation (Hooker et al., 1970; Wheeler et al., 1971; Arntzen et al., 1973b), swelling and other changes in mitochondria (Miller and Koeppe, 1971; Gegenbach et al., 1973), ion leakage from roots and leaves (Arntzen et al., 1973; Gracen et al., 1972; Garraway, 1973; Halloin et al., 1973), and uncoupling of oxidative phosphorylation (Miller and Koeppe, 1971; Peterson et al., 1975). Arntzen et al. (1973a, 1973b) reported that the pathotoxin induced stomatal closure, followed by inhibition of photosynthesis and reduction of the ATP concentration. Mertz and Arntzen (1973) found depolarization of the membrane electrical potential. Tipton et al. (1973) measured an inhibition of K^+-dependent ATPase. Garraway (1973) found leakage of peroxidase with Tcms cytoplasm after inoculation with race T. In none of these cases did the N cytoplasm show similar effects.

On the basis of these observations, several authors (Arntzen et al., 1973b; Halloin et al., 1973) concluded that membranes might be either the primary or secondary site of pathotoxin effects (Gracen et al., 1972; Halloin et al., 1973). Specific effects on mitochondrial membranes have been reported in an early step of the electron-transport chain, preceding entry of electrons from succinate dehydrongenase, which represents the first ATP-coupled site associated with the endogenous NADH dehydrogenase (Peterson et al., 1975).

There is some evidence in the literature that the membranes of Tcms and N cytoplasm might differ in certain intrinsic properties, especially membrane permeability. Halloin et al. (1973) reported a rate of carbohydrate leakage in Tcms leaves had a 15% higher rate of carbohydrate leakage than did N leaves. In the absence of toxin, Arntzen et al. (1973b) found a slightly higher (nonsignificant) ^{32}P leakage in Tcms roots and a slightly higher ^{32}P uptake by untreated Tcms mitochondria.

The findings resulting from the experimental work reported here show differences unassociated with pathotoxin effect in the N and Tcms cytoplasms. A differential exists between the two cytoplasms and is exhibited by the difference in their capacity to absorb phosphorus from a neutral solution of ammonium tripolyphosphate applied to the leaves.

2. Materials and methods

The two genotypes, Nrf_1rf_1 and $Tcmsrf_1rf_1$, of the corn inbred B37 used in this experiment are essentially isolines and differ only in their cytoplasm, N and Tcms. Seeds were planted in well-fertilized soil in No. 10 cans in the greenhouse on July 31, 1972. Quantities of 0 (control), 170 microgram P as orthophosphate and 218 microgram P as tripolyphosphate, were applied on August 30 in a volume of 25 microliters of solution to a circular area of 1.2 cm diameter on the youngest mature leaf surface. The circular delineations were made by the wax treatment described previously. All solutions contained a surfactant (0.1% Tween-80) to lower the surface tension and were neutralized to pH 7.0 with ammonium hydroxide. There were 20 replications per treatment, and the experiment was arranged as a randomized complete block design with 10 blocks. Samples were taken 24 hours and 12 days after application of the solutions and were analyzed according to the usual methods. Ten of the replications were sampled at each sampling time.

3. Results and discussion

Table 34 shows the means of the phosphorus analyses of the leaf washings and discs and the calculated quantities of

Table 34. Absorption and translocation of phosphorus of orthophosphate and tripolyphosphate by normal and Tcms cytoplasm of one inbred line of corn in 1-day and 12-day sampling times[a]

Cytoplasm	Length of experiment (days)	P in leaf washing (µg)	P in leaf disc (µg)	P absorbed as % of applied P	% T>N	P translocated as % of absorbed P
			Control (0.1% Tween-80)			
Normal	1	0.69	17.73			
Tcms	1	0.77	16.52			
Normal	12	0.75	15.93			
Tcms	12	0.93	15.59			
			Orthophosphate			
Normal	1	79.49	63.07	53.7	-4.5	49.8
Tcms	1	83.65	60.65	51.3		49.0
Normal	12	5.57	41.68	97.2	0.3	84.4
Tcms	12	5.13	45.39	97.5		82.1
			Tripolyphosphate			
Normal	1	211.03	23.49	3.7	159.5	28.0
Tcms	1	198.20	29.44	9.6		37.9
Normal	12	129.03	39.72	41.2	54.9	73.4
Tcms	12	80.02	50.38	63.8		74.7

[a]Each value represents the average of 10 replicates.

absorbed and translocated phosphorus. Table 35 gives the analyses of variance for the percentage of the added phosphorus absorbed and for the percentage of the absorbed phosphorus translocated from the treated area.

Table 35. Analyses of variance for phosphorus absorption and translocation

Source	d.f.	Mean squares: P absorption	Mean squares: P translocation
Blocks	9	34.24	59.42
Cytoplasms (A)	1	875.03**	78.25
P treatments (B)	1	41218.51**	3294.32**
Sampling times (C)	1	41121.47**	28106.80**
A x B	1	1164.92**	259.36
A x C	1	472.29**	129.00
B x C	1	5.55	266.79
A x B x C	1	241.98**	64.10
Error	63	31.13	79.27

**Significant at 1% level.

a. Phosphorus absorption Statistically, the phosphorus absorption is significantly different for all three main effects: cytoplasms, phosphorus treatment, and sampling time. Each cytoplasm had a greater uptake of phosphorus from orthophosphate than from tripolyphosphate

tripolyphosphate at both 1 day and 12 days after addition of the phosphate solutions. The phosphorus absorption is in all instances significantly greater after 12 days than after 1 day. Because of the statistically significant two-factor interactions, cytoplasm by phosphorus treatment and cytoplasm by sampling time, and the three-factor interaction, the simple effects with respect to differences in cytoplasms, should be considered.

The simple effects listed in Table 36 indicate that the T cytoplasm has a significantly greater absorption of phosphorus from tripolyphosphate for both sampling times (159.5%, 1 day; 54.9%, 12 day) than does the N cytoplasm. No difference between the cytoplasms in absorption of phosphorus from orthophosphate is evident, however, indicating that membrane permeability is not limiting the phosphorus uptake mechanism (carrier) with the orthophosphate. The greater absorption of tripolyphosphate (a larger molecule with a larger negative charge than that of orthophosphate) by the T cytoplasm suggests a difference in the intrinsic properties between the membranes of Tcms and N cytoplasms.

b. <u>Phosphorus translocation</u> Table 35 shows a significant difference in phosphorus translocation between the two phosphates and between sampling times, but not between the cytoplasms (Table 35, line 2).

The difference between the two compounds in phosphorus translocation seen at the 1-day sampling time disappeared by

12 days. The explanation is presumably that there was a greater original concentration gradient of orthophosphate than of tripolyphosphate with both cytoplasms, leading to a greater driving force for translocation of orthophosphate. This explanation is consistent with the finding, reported in previous pages, that, within a given variety of corn, the percentage of the absorbed phosphorus translocated from the treated area was substantially independent of the form and concentration of phosphorus applied. Thus, the difference in behavior of the two phosphates between the cytoplasms does not reside in phosphorus translocation, but in differential absorption.

4. Conclusion

The absorption of foliar applied tripolyphosphate was significantly greater in cytoplasmic male-sterile (Tcms) plants than in plants having normal (N) cytoplasm. There was no significant difference in orthophosphate absorption between Tcms and N cytoplasm, nor was there any significant difference in the translocation of either source of phosphorus inside the plant as indicated by measurements of translocation over the 12-day period. The differential uptake of the tripolyphosphate by the Tcms and N cytoplasm is believed related to membrane permeability.

Table 36. Mean squares and F-values of the simple effects of phosphorus absorption

Comparisons between cytoplasms	Mean squares	F
Within orthophosphate for 1 day	28.77	<1
Within orthophosphate for 12 days	0.66	<1
Within tripolyphosphate for 1 day	174.55	5.61+
Within tripolyphosphate for 12 days	2550.25	81.92**

+,**Indicate significance at 2% and 1% levels, respectively.

VI. SPRAYING OF WHOLE PLANTS IN THE GREENHOUSE

A. Determination of Maximum Allowable Phosphorus Spray Concentration in the Greenhouse, Experiment 12

1. Introduction

From Experiment 10 it was learned that the amount of damage might be affected by the way the application is done. It was therefore decided to do some preliminary tests to determine the concentration of phosphorus that could be applied to plants in the greenhouse by spraying before the main spraying experiment was done.

2. Procedure

On June 25, 1972, solutions of various phosphorus compounds at different concentrations were sprayed with a small hand-pump sprayer equipped with a fine nozzle on three corn and three soybean plants. All solutions contained 0.1% Tween-80. The plants were sprayed so that both sides of the leaves were wet and dripping occurred. Estimates of damage to the leaves, considering only the three most damaged leaves, were made 10 days after application.

3. Results and discussion

Table 37 gives visual estimates of damage to the leaves of corn and soybeans that were sprayed with different concentrations of solutions of various phosphates. The approximate maximum additions are shown also, the assumption being that

Table 37. Estimates of damage to leaves of corn and soybeans 10 days after foliar application of different concentrations of various sources of phosphorus, and approximate concentrations that could be applied with damage to no more than 5% of the leaf area

Source of phosphorus	pH	P in solution applied, %	Estimates of damage to leaves[a]		Approximate maximum addition, %	
			Corn	Soybeans	Corn	Soybeans
Ammonium ortho-phosphate	7.0	0.28	0	0	0.5	0.3
		0.50	3	10		
		0.62	2	15		
		0.74	10	20		
		0.87	15	25		
		1.40	25	50		
Ammonium pyro-phosphate	7.0	0.74	2	7	0.8	0.7
		0.99	10	17		
		1.12	15	22		
		1.49	20	30		
Ammonium tripoly-phosphate	8.3	1.24	1-2	2	1.4	1.0
		1.49	6	20		
		1.86	15	30		
		2.23	17	30		
Ammonium tetrapoly-phosphate	8.1	1.12	2	1	1.3	1.2
		1.24	4	5		
		1.49	12	25		
		1.86	16	30		
Ammonium trimeta-phosphate	7.0	1.24	5	0	1.3	1.2
		1.49	15	40		
		1.86	65	50		
		2.23	70	60		
Ammonium tetrameta-phosphate	7.0	1.24	1	0	1.4	1.3
		1.49	5	7		
		1.86	7	20		
		2.23	12	25		

[a]Means of three most damaged leaves per plant in three replications. Values represent the percentage of the leaf area.

Table 37. (Continued)

Source of phosphorus	pH	P in solution applied, %	Estimates of damage to leaves[a]		Approximate maximum addition, %	
			Corn	Soybeans	Corn	Soybeans
Ammonium polyphosphate mixture	7.0	0.87	7	13	0.9	0.7
		1.12	15	25		
		1.49	50	50		
Na-Churs product	7.0	0.74	12	5	0.7	0.6
		0.87	7	9		
		1.12	22	13		
		1.49	42	25		
		1.86	46	40		

visual damage to a maximum of 5% of the leaf area is acceptable. The 5% limit is quite arbitrary and is subject to experimental verification.

B. Response of Plants to Spraying with Solutions of Various Phosphates in the Greenhouse, Experiment 13

1. Introduction

After the discovery that certain condensed phosphates could be applied at much higher concentrations than orthophosphate and that some were well absorbed and translocated, the next step seemed to be to spray whole plants to determine whether this type of phosphorus nutrition would be adequate for plant growth and how it would affect plant growth.

The most common measurements of plant responses to soil fertility treatments are total plant weight and grain yield.

In some circumstances, conducting field experiments is the most desired method of testing possible responses. Extensive field testing of the condensed phosphates, however, would require several kilograms of each compound, which could not easily be produced with the available laboratory scale facilities. It therefore was decided to dc a greenhouse experiment, in which individual plants were sprayed, and a small-scale field experiment. The total amount of product required for both experiments did not exceed 1 kilogram per compound.

2. Procedure

Soybeans of the Hark variety were planted on May 27, 1972, in No. 10 cans which contained 3 kg of a mixture by volume of two parts of low phosphorus soil[1], one part of sand, and one part of peat. The soil was thoroughly mixed with 200 ppm of nitrogen and 100 ppm of potassium as potassium nitrate and ammonium nitrate. No phosphorus was added to the soil because the aim was to grow healthy, slightly phosphorus-deficient plants.

Corn was planted on May 29 in plastic wastebaskets, which contained 12 kg of soil. The soil mixture and fertility were

[1]Low phosphorus soil, Webster silt loam, was obtained from the Bruner farm, 5 miles west of Ames. The following soil-test values were found by the Iowa State Soil Testing Laboratory: pH = 6.5, available potassium = 86 lb/acre, and available phosphorus = 10 lb/acre.

the same as described for soybeans. A soil phosphorus treatment was initiated by planting both crops in a soil mixture similar to the one described above but containing an additional 80 ppm of phosphorus as monobasic potassium phosphate.

Both crops looked very phosphorus-deficient on June 15, and it was decided to apply 20 ppm of phosphorus in the form of ammonium orthophosphate to all plants except eight corn plants. These eight cultures were left in the phosphorus-deficient condition and were designated the "low soil phosphorus treatment."

The first phosphorus spray was applied on June 28, when the corn plants had seven leaves and the soybeans six leaves. The phosphorus solutions were sprayed with a small hand-pump sprayer at night as 200 ml of solutions to 16 corn plants and 16 soybean plants. Leaves were sprayed on both sides. The humidity in the greenhouse was raised close to saturation by closing all the windows and running the water sprinkler system under the greenhouse benches all night.

The experiment was set up as a randomized block design with sub-blocks of unequal size. The experimental unit was one plant in one pot. There were eight blocks with three sub-blocks per block.

Sub-block one contained one treatment for the soybeans (80 ppm of phosphorus applied to the soil) and two treatments for the corn (80 ppm of phosphorus applied to the soil and the low soil phosphorus treatment). Sub-block two contained the eight phosphorus spray treatments listed in Table 38 plus a control spray treatment (0.1% Tween-80). There were two applications of the sprays. Sub-block three contained the same treatments as sub-block two, but there were three applications of the sprays.

Thirteen days after the first spray treatment, leaf samples were taken from the unsprayed youngest mature leaf by removing three leaf discs of 1.8 cm^2 with a cork borer. The samples were dried at 65^oC, weighed, and analyzed for total phosphorus according to methods described earlier.

The second spray application was made on July 17 by spraying 1500 ml of solution on the 16 soybean plants and the 16 corn plants. All plants received 20 ppm of potassium and 50 ppm of nitrogen on July 20. A second leaf sampling of unsprayed young leaves was taken on July 27.

The plants in sub-block three were sprayed on July 31 for the third time with a total volume of 750 ml of solution. The ears of the corn plants were covered with a plastic bag to protect the silk and husk leaves from the phosphorus solutions.

All plants received nutrient solutions containing 25 ppm of potassium and 50 ppm of nitrogen as potassium nitrate and ammonium nitrate on August 3, 14, and 22.

Leaf samples of sub-block three were taken on August 18 by cutting the tops of three to five of the unsprayed husk leaves. The soybeans were not sampled because vegetative growth had stopped, and unsprayed leaves could not be collected.

Table 38. Phosphorus concentrations and pH of the three spray solutions applied in Experiment 13

Forms of phosphorus applied[a]	P in spray solution, % 1st	2nd	3rd	pH of spray solution
Orthophosphate	1.17	0.73	0.61	7.0
Pyrophosphate	0.58	0.77	0.63	8.5
Tripolyphosphate	0.95	1.16	0.96	8.5
Tetraphosphate	0.99	1.14	0.92	8.0
Trimetaphosphate	0.83	1.65	1.28	7.0
Tetrametaphosphate	0.94	1.57	1.19	7.0
Polyphosphate mixture	1.05	1.29	0.92	7.0
Na-Churs product	0.42	0.61	0.52	7.0

[a]All except Na-Churs product were applied as neutral solutions of the ammonium salts.

The greenhouse was periodically fumigated with Parathion gas, which was alternated with plant sprays of Malathion, Kelthane, and Morestan to control thrips, lice, and red spider mites.

Watering of the soybeans was stopped after September 5, and the corn did not receive any water after September 14. Shortly thereafter, the individual plants were harvested.

3. Results and discussion

At the time of spraying, small aliquots of the solutions were saved and used for phosphorus determinations. The values, as means of three replicate analyses, are given in Table 38. Ammonium orthophosphate was accidentally applied at twice the intended concentration and damaged up to 10 percent of the leaf area on both crops.

At the time of the second spray application on July 17, the plants were much older, and it was thought that the phosphorus concentrations could be increased to the values found permissible for soybeans in Experiment 12. The three days following July 17 were very hot, with temperatures up to 107°F in the greenhouse, and significant leaf damage occurred with several compounds. Estimates of damage to the leaves were made on July 27 and are given in Table 40 for soybeans and in Table 43 for corn. The soybeans were damaged by tripolyphosphate, and the corn by trimetaphosphate and the polyphosphate mixture. Because of the damage related to the second spraying, the concentrations of all compounds applied to sub-block 3 in the third spraying were lowered.

a. Soybeans The data on yields of dry matter and yields of phosphorus were subjected to an analysis of variance. Duncan's multiple-range test was then applied to the statistically significant "F" values. Correlations were computed wherever they were considered helpful for presentation and discussion of the data.

Appendix Table 66 gives the means of three variables, seed weight, seed count, and 100-seed weight, which might have been affected by the number of spray treatments. Table 39 gives the F-values and their possible significance. It appeared that the phosphorus applications had significant effects on these three variables. When the data of sub-block 2 and 3 were analyzed as a split-plot experiment, however, there was no significant difference among the number of spray treatments. Thus it is not necessary to keep them apart.

The means over all replications of sub-blocks 2 and 3 are given in Table 40, together with the sample weight, phosphorus content, and percentage phosphorus in the leaf samples taken 14 days after the first and second spray treatment. These were samples of newly grown leaves that were not present when the plants were sprayed. The F-values of the analyses of variance in a completely randomized block experiment with eight blocks are given in Table 41. The total sum of squares for treatments is divided into two orthogonal comparisons, the F-values for which are also listed in Table 41. Most of the F-values are significant at the 1% level. The F-values for the phosphorus content and phosphorus percentage in the leaves for the soil versus spray treatments of phosphorus, however, are not significant at the second sampling. Significant differences among the phosphorus spray treatments occur with all the measurements, which justifies the Duncan tests given in Table 40. Simple correlation coefficients are given in Table 42.

Table 39. F-values of analyses of variance of yield, number of seeds, and 100-seed weight of soybeans in Experiment 13

Source of variation	d.f.	Yield	Number of seeds	100-seed weight
		F-values and significance		
Blocks	7	2.89**	3.36**	3.10**
Applications	18	10.16**	7.95**	2.84**
Soil P vs spray P	1	44.38**	41.64**	1.44**
Error	134			
Among spray applications	17	7.91**	6.07**	3.23**
Number of sprays (A)	1	<1	<1	<1
Error (a)	(7)			
P compounds (B)	8	14.72**	9.94**	4.88**
A x B	8	2.08*	2.95**	1.97*
Error (b)	112			
Coeff. of variation:		8.56	7.42	7.32

*,**Indicate significance at 5% and 1% levels, respectively.

Table 40. Yield, seed number, phosphorus content of leaf samples, and estimates of the damage of treatments to the leaves of soybeans in Experiment 13

Treatment[b]	Yield (g/plant)	Seed number	100-seed weight (g)	First leaf: Dry wt per disc (mg)	First leaf: P content per disc (μg)
Control	21.0 f[c]	170 f	12.39 ab	19.4 a	55.31 e
Orthophosphate spray	25.4 bc	201 bcd	12.64 a	15.8 c	62.30 bcd
Pyrophosphate spray	22.9 de	193 de	11.90 bc	17.6 b	58.75 de
Tripolyphos-phate spray	21.5 ef	188 e	11.40 c	18.3 b	63.81 bc
Tetrapolyphos-phate spray	26.1 b	206 bc	12.69 a	17.3 b	60.03 bcd
Trimetaphos-phate spray	24.2 cd	194 cde	12.54 ab	16.0 c	59.64 cde
Tetrapolyphos-phate spray	25.0 bc	199 bcde	12.59 ab	15.2 c	58.16 de
Polyphosphate mixture spray	26.3 b	205 bcd	12.84 a	15.2 c	64.29 b
Na-Churs spray	26.5 b	207 b	12.84 a	15.0 c	59.22 de
Orthophosphate in soil	28.0 a	221 a	12.71 a	17.4 b	82.66 a

[a]Estimates of damage to the leaves are the percentages of the total area of the three most damaged leaves that were either dead or yellow as indicated.

[b]All the spray treatments except Na-Churs were applied as neutral solutions of the ammonium salts.

[c]Means in a given column not followed by one or more common letters are statistically different at the 5% level.

sampling	Second leaf sampling			Estimates of damage to leaves[a]	
% P in leaf discs	Dry weight per disc (mg)	P content per disc (μg)	% P in leaf disc	Area dead %	Area yellow %
.288 f	18.6 b	64.97 d	.353 d	0.0 f	0.0 b
.398 bc	18.4 b	80.16 abc	.439 b	5.5 b	4.4 a
.335 e	20.1 a	81.56 ab	.408 bc	4.8 bc	1.6 b
.350 de	16.8 c	84.76 a	.509 a	8.9 a	4.3 a
.353 de	19.6 ab	78.46 bc	.400 bc	2.1 e	4.4 a
.375 cd	18.5 b	80.22 abc	.436 b	4.4 cd	5.4 a
.384 cd	19.5 ab	84.67 a	.437 b	2.3 e	0.4 b
.423 b	20.2 a	81.99 ab	.409 bc	3.6 d	4.3 a
.400 b	19.0 ab	74.44 c	.393 c	2.4 e	1.3 b
.479 a	19.9 a	80.58 ab	.407 bc	0.0 f	0.0 b

Table 41. F-values of analyses of variance of phosphorus determinations in leaf samples and estimates of damage of treatments to leaves of soybeans in Experiment 13

		F-values and significance level							
		1st leaf sampling			2nd leaf sampling			Estimates of damage to leaves	
Source of variation	d.f.	Dry wt per disc	P content per disc	% P	Dry wt per disc	P content per disc	% P	Area dead	Area yellow
Blocks	7	1.08	<1	<1	3.12**	<1	1.26	1.30	1.53
Treatments	9	14.16**	26.46**	18.09**	7.01**	8.99**	11.42**	58.00**	17.33**
Soil P vs spray P	1	2.95+	208.05**	74.63**	5.20*	<1	1.16	104.07**	28.60**
Among P compounds	1	15.54**	3.75**	11.00**	7.24**	10.04**	12.70**	51.61**	15.92**
Error	143								
Coeff. of variation		9.45	9.48	12.98	8.32	9.79	11.49	41.33	78.84

+,*,**Indicate significance at 10%, 5%, and 1% levels, respectively.

Table 42. Coefficients of simple correlation among yield, number of seeds, 100-seed weight, leaf analyses, and estimates of damage to the leaves of soybeans in Experiment 13[a]

				First leaf sampling			Second leaf sampling			Estimates of damage to leaves	
	Yield	No. of seeds	100-seed wt	Dry wt per disc	P content per disc	% P	Dry wt per disc	P content per disc	% P	Area dead %	Area yellow %
Yield	1.000	.756**	.572**	-.349**	.314**	.469**	.333**	.114	-.169*	-.245**	-.003
No. of seeds		1.000	-.100	-.235**	.386**	.441**	.095	.162*	.045	-.085	-.006
100-seed wt			1.000	-.238**	-.010	.158*	.399**	-.027	-.322**	-.277**	-.009
Dry wt per disc (1st l.s.)				1.000	.022	-.640**	-.048	-.220**	-.138+	-.062	-.092
P content per disc (1st l.s.)					1.000	.741**	.037	.151+	.112	-.144+	-.146+
% P (1st l.s.)						1.000	.061	.250**	.165*	-.086	-.056
Dry wt per disc (2nd l.s.)							1.000	.149+	-.581**	-.339**	-.090
P content per disc (2nd l.s.)								1.000	.710**	.322**	-.199*
% P (2nd l.s.)									1.000	.530**	.229**
% of leaf area dead										1.000	.481**
% of leaf area yellow											1.000

[a]Correlations are based on 158 degrees of freedom.

+,*,**Indicate significance at 10%, 5%, and 1% levels, respectively.

Table 43. Mean values of characteristics of corn plants measured in Experiment 13[a]

Treatment[c]	Yield (g/plant)	Kernels per plant	100-seed weight (g)	Plant height (cm)
Control (0.1% Tween-80)	108.2 b	386 b	28.3 cd	263 cd
Orthophosphate spray	105.9 b	350 cd	30.3 ab	256 bc
Pyrophosphate spray	107.3 b	364 bc	29.6 abc	260 abc
Tripolyphosphate spray	106.1 b	361 bc	29.6 abc	253 cd
Tetrapolyphosphate spray	105.7 b	348 cd	30.4 a	254 cd
Trimetaphosphate spray	94.0 c	321 e	29.3 abc	257 bc
Tetrametaphosphate spray	103.3 b	361 bc	28.7 bcd	258 abc
Polyphosphate mixture spray	95.6 c	331 de	29.0 abc	247 d
Na-Churs spray	110.2 b	183 b	28.8 abcd	263 ab
Orthophosphate in soil	118.1 a	433 a	27.3 d	265 a
Low-phosphate soil	36.6[d]	216[d]	16.9[d]	253 cd

[a]Means in a given column not followed by one or more common letters differ significantly at the 5% level.

[b]Leaf directly under ear.

[c]All the sprays except Na-Churs were applied as neutral solutions of the ammonium salts.

[d]Mean of two observations.

Leaf width[b] (cm)	Top weight (g)	Root weight (g)	Cob weight (g)	Total plant wt (g)	Top-root ratio
8.6 a	83.2 b	16.7 bc	19.7 b	228.0 b	14.0 ab
8.1 bc	78.6 bc	15.6 cd	18.1 b	218.1 b	14.6 ab
8.3 abc	85.0 b	17.5 bc	19.5 b	229.3 b	13.4 b
8.3 abc	83.9 b	19.3 b	18.6 b	227.8 b	12.8 b
8.2 bc	78.2 bc	16.7 bc	18.3 b	218.9 b	13.6 b
8.2 bc	72.2 cd	13.7 de	14.8 c	194.7 c	14.5 ab
8.2 bc	79.1 bc	16.1 cd	18.3 b	216.8 b	14.4 ab
8.0 b	72.7 cd	13.3 de	16.1 c	197.6 c	15.8 a
8.4 ab	81.6 b	16.1 cd	19.1 b	227.0 b	14.7 ab
8.4 ab	114.0 a	30.1 a	24.5 a	286.7 a	9.8 c
7.2 d	67.9 d	10.9 e	8.6 d	107.1[d]	11.7[d]

Table 43. (Continued)

Treatment	First leaf sampling		
	Dry wt per disc (mg)	P content per disc (μg)	% P in leaf discs
Control (0.1% Tween-80)	24.3 a	61.87 b	.256 e
Orthophosphate spray	22.4 b	59.45 bcd	.268 e
Pyrophosphate spray	18.9 ef	54.75 e	.291 d
Tripolyphosphate spray	20.5 c	58.45 cd	.286 d
Tetrapolyphosphate spray	19.1 def	59.10 bcd	.310 bc
Trimetaphosphate spray	18.4 def	58.77 cd	.319 b
Tetrametaphosphate spray	19.0 def	56.70 de	.298 cd
Polyphosphate mixture spray	19.7 cde	59.45 bcd	.303 bcd
Na-Churs spray	20.1 cd	60.37 bc	.301 cd
Orthophosphate in soil	23.2 b	82.78 a	.357 a
Low-phosphate soil	20.1 cd	33.84 f	.169 f

[e]Estimates of damage to the leaves are the percentages of the total area of the three most damaged leaves that were either dead or yellow as indicated.

Second leaf sampling			% P in leaf disc at third sampling	Estimates of damage to the leaves[e]	
Dry wt per disc (mg)	P content per disc (µg)	% P in leaf discs		Area dead %	Area yellow %
20.7 bc	64.61 e	.313 cd	.089 c	0.0 ef	0.0 d
20.3 bc	68.91 cde	.340 ab	.133 a	8.3 c	0.9 d
21.2 b	68.07 cde	.324 bc	.118 ab	0.2 ef	0.0 d
21.1 b	72.02 bc	.344 ab	.100 b	0.6 ef	0.6 d
20.9 b	67.63 cde	.324 bc	.127 a	5.0 d	5.9 b
21.1 b	72.86 bc	.346 ab	.136 a	24.1 a	12.8 a
20.8 bc	70.04 bcd	.338 ab	.136 a	2.5 def	4.1 c
20.8 bc	74.70 b	.361 a	-	13.9 b	11.6 a
19.8 c	65.30 de	.331 bc	.126 a	2.8 de	1.3 d
23.1 a	80.41 a	.347 ab	.259 a	0.0 ef	0.0 d
16.1 d	46.54 f	.290 d	-	0.0 ef	0.0 d

The plants receiving a soil application of phosphorus had a significantly higher yield than the plants receiving any of the phosphorus spray treatments. This finding indicates that two or even three phosphorus spray treatments on low-phosphorus soybeans grown in the greenhouse did not supply as much phosphorus to the plants as a soil that received 80 ppm of phosphorus as fertilizer. Nevertheless, as a group, the plants receiving the spray applications of phosphorus had a significantly higher yield than the control. The range was from a very small increase with tripolyphosphate, which damaged the leaves, to relatively large increases with tetrapolyphosphate, the polyphosphate mixture, and Na-Churs product, which were almost as great as the increase in yield obtained with the soil application of phosphorus.

The phosphorus percentages in the discs cut from the leaves of the control plants were high enough to suggest that phosphorus was not a major limiting factor. deMooy et al. (1973) described phosphorus percentages in the youngest mature leaf from 0.16 to 0.25% as low and from 0.26 to 0.50% as sufficient.

The 100-seed weight of soybeans, which is normally little affected by soil fertility treatments, and the number of seeds per plant are significantly lower with the tripolyphosphate spray treatment than with the other spray treatments, confirming the damaging effect of the second spray on the yield. It was also observed on August 8 that the plants sprayed with ortho-, pyro-, tripoly-, and trimetaphosphate solutions, which produced the most damage to the leaves (Table 40), had more yellow leaves than the other plants.

The percent phosphorus of the first leaf sampling of the soil phosphorus treatment is significantly higher than all other treatments, and all phosphorus treatments are higher than the control. The tripolyphosphate treatment is the winner at the time of the second sampling.

The dry weights per leaf sample permit a comparison among treatments on the basis of equal surface area per sample. Different weights probably indicate different contents of soluble and stored carbohydrate because it seems unlikely that the leaf thickness would change after the leaf is full grown. The weights of the leaf discs are negatively correlated with the phosphorus percentages in the discs at both samplings. Because the leaf discs were cut from newly matured leaves that were produced after the plants had been sprayed with the phosphate solutions, because the new growth is produced in large degree by translocation of constituents from the old growth, and because the phosphate treatments increased the yield of grain, the indications are that the phosphorus treatments promoted development of a greater area of new leaf growth. In time, the new growth from the phosphate-treated plants would be expected to develop as great a weight per unit leaf area as would be found in the controls.

b. <u>Corn</u> Appendix Table 67 gives the means of measurements that depend on the number of spray treatments. Tables 44 and 45 give the F-values of the analyses of variance of these measurements. Table 44 contains F-values for measurements of characteristics for which there were experimental observations on plants grown on the low-phosphorus soil. Table 45 contains F-values for measurements of characteristics for which there were no observations on plants grown on the low-phosphorus soil. Table 46 contains the F-values for measurements of characteristics that were independent of the number of sprays. There were no observations for the third leaf sampling of two treatments, and for this reason the phosphorus percentages in the third leaf sampling are listed with a reduced number of degrees of freedom.

The effects of phosphorus applications or treatments are significant for all variables. When the orthogonal comparison of soil-applied phosphorus vs low-phosphorus soil is separated from the total sum of squares for applications or treatments, the difference is highly significant for all characteristics except for damage to the leaves, which was zero in both instances. The orthogonal comparison of orthophosphate applied to the soil vs phosphates applied as sprays is highly significant for all variables except the width of the leaf directly under the ear, the 100-seed weight, and the percentage content of phosphorus in the leaf discs of the second leaf sampling. The differences among effects of phosphorus sprays

Table 44. F-values of analyses of variance of measurements of certain characteristics of corn plants in Experiment 13[a]

Source of variation	d.f.	F-values and significance level				
		Plant height	Leaf width	Top weight	Root weight	Cob weight
Blocks	7	1.38	1.71+	1.97+	4.37**	5.20**
Applications	19	3.33**	4.19**	15.06**	13.79**	13.75**
Soil P vs low-P soil	1	7.86**	44.54**	138.57**	138.64**	201.94**
Soil P vs spray P	1	9.21**	1.78	210.78**	199.23**	90.13**
Error	141					
Among spray applications	17	3.65**	1.66*	4.59**	2.60**	3.93**
Number of sprays (A)	1	6.52*	<1	7.42*	<1	1.36
Error (a)	(7)					
P compounds	8	5.44**	2.46*	5.95**	4.26**	7.39**
A x B	8	1.14	1.02	<1	1.25	<1
Error (b)						
Coeff. of variation		3.76	5.14	11.01	21.81	14.23

[a]Characteristics included in this table are the ones for which there were experimental observations on plants grown on the low-phosphorus soil.

+,*,**Indicate significance at 10%, 5%, and 1% levels, respectively.

Table 45. F-values of analyses of variance of measurements of certain characteristics of corn plants in Experiment 13[a]

Source of variation	d.f.	F-values and significance level				
		Yield of grain	Kernel count	100-seed weight	Total plant wt	Top-root ratio
Blocks	7	2.69*	1.20	1.03	4.02**	3.72**
Applications	18	5.19**	8.09**	2.01*	18.03**	3.92**
Soil P vs spray P	1	35.82**	78.05**	13.49	240.24**	43.00**
Error	134					
Among spray applications	17	4.66**	4.89**	1.40	6.12**	1.57+
Number of sprays	1	<1	<1	<1	1.56	1.44
Error (a)	(7)					
P compounds	8	8.70**	8.25**	1.93+	11.79**	1.87+
A x B	8	1.21	2.10*	<1	<1	1.14
Error (b)	112					
Coeff. of variation		8.44	9.14	7.33	7.53	18.62

[a]Characteristics included in this table are the ones for which there were no experimental observations on plants grown on the low-phosphorus soil.

+,*,**Indicate significance at 10%, 5% and 1% levels, respectively.

Table 46. F-values of analyses of variance for certain characteristics of leaves of corn in Experiment 13[a]

Source of variation	d.f. col. 3-10	Estimated damage to leaves: Area dead	Estimated damage to leaves: Area yellow	F-values, First leaf: Dry wt per leaf disc	F-values, First leaf: P content per leaf disc
Blocks	7	2.02+	1.84+	1.06	<1
Treatments	10	75.59**	65.36**	33.47**	101.90**
Soil P vs low-P soil	1	<1	<1	26.86**	895.64**
Soil P vs spray P	1	48.63**	45.48**	70.34**	582.28**
Error	150				
Among spray treatments	8	74.39**	63.70**	32.52**	5.03**
Error	143				
Coeff. of variation		63.48	65.63	6.49	6.31

[a]Characteristics included in this table are the ones that are independent of the number of sprays applied.

+,*,**Indicate significance at 10%, 5%, and 1% levels, respectively.

and significance levels					
sampling	Second leaf sampling				F value and sig. level of % P in leaf disc in 3rd leaf sampling
% P in leaf disc	Dry wt per leaf disc	P content per leaf disc	% P in leaf disc	d.f. col. 12	
1.84+	2.00+	<1	21	7	<1
47.52**	13.96**	16.92**	4.66**	8	20.50**
373.04**	126.78**	136.34**	18.51**		
118.28**	40.41**	39.23**	2.09	1	<1
12.48**	1.51	5.39**	3.82**	7	23.05**
				64	
7.69	6.90	9.66	9.26		21.71

are significant with all characteristics except the 100-seed weight. When sub-blocks 2 and 3 were statistically analyzed as if they represented a split-plot experiment with the numbers of sprays as main plots, the analyses of variance indicated that the height of the plants and the dry weight of the tops were greater, at the 5% significance level, in plants that received three sprays than in those that received two. Table 43 gives the means, over all 16 replications, of all the characteristics measured in this experiment. The Duncan tests of significance are included also.

One of the objectives of this experiment, to grow a crop to maturity and measure yields, was not accomplished so well with corn as with soybeans because of poor pollination in the greenhouse. Most cobs had only 1/2 to 2/3 of the maximum number of kernels possible, an observation that is suggested also by the numbers of kernels per plant. The poorest results were obtained with plants on the low-phosphorus soil. These plants silked later than the others, and only two of the plants had grain on the ear. The performance of plants sprayed with the trimetaphosphate and polyphosphate mixture and perhaps others was inhibited by damage to the leaves from the sprays.

The yield of grain from plants receiving the soil application of phosphorus is significantly higher than that of plants receiving any other treatment. There is no significant difference between the yield of grain from the plants on the control and the phosphorus spray treatments except that the plants sprayed with solutions containing the trimetaphosphate and polyphosphate mixture had lower yields. The phosphorus content of the leaf discs obtained in the first and second sampling of the leaves of the control indicates that the plants were not really phosphorus deficient. The critical value, which is the concentration below which yield decreases or deficiency symptoms appear, is given by Jones and Eck (1973) as 0.23 to 0.295%. Plants grown on the low-phosphorus soil, however, were clearly deficient in phosphorus, and the leaf discs had the lowest phosphorus contents of all.

With none of the phosphorus treatments did the leaf width exceed that of the control plants. The leaf width of plants on the low-phosphorus soil, however, was significantly less than the leaf width of the control plants, which indicates a deficiency of phosphorus for plant growth in the low-phosphorus soil.

Application of phosphorus to the soil produced the highest top weight, root weight, cob weight, seed weight, seed count, and total dry plant weight, but the lowest 100-seed weight and top-root ratio. The high root weight and the low top-root ratio observed with orthophosphate applied to the soil confirm the known fact that the plant organs closest to the source of a limiting factor are least affected by the deficiency and benefit most from additions.

The leaf discs from newly developed, unsprayed leaves from plants previously sprayed with phosphate solutions had higher phosphorus contents at all three leaf samplings than did leaf discs from the control plants and the plants grown on the low-phosphorus soil but not as high as those from plants grown on soil treated with orthophosphate. The phosphorus percentages in the leaf discs obtained in the third leaf sampling, for which the husk leaves were used, followed the same trends as were observed in the first and second samplings but showed much greater variability among replications (coefficient of variation = 21.7%) and had much lower absolute values than the regular leaves.

The phosphorus content of the first leaf sampling has the highest correlation with grain yield ($r = 0.37$) of all the variables involving plant phosphorus analyses, as can be seen in Table 47. The phosphorus percentages in the leaves were relatively low at this sampling time.

The weights of leaf discs at the first and second sampling are correlated positively with the top and root weights.

The estimates of damage to the leaves from the various phosphate sprays are negatively correlated with all measurements of plant growth. Although the correlations are not high, their consistency confirms the importance of maintaining at a low level the damage to leaves from phosphorus-bearing sprays.

Plants receiving the sprays of Na-Churs product were about like the controls in most characteristics. The phosphorus percentages in the leaf discs, however, exceeded those in the discs cut from leaves of the control plants.

Table 47. Correlation coefficients among measured characteristics of corn in Experiment 13[a]

	% of leaf area dead	% of leaf area yellow	Plant height	Leaf width	Top weight	Root weight
% of leaf area dead	1.00	.75**	-.21**	-.04	-.37**	-.35**
% of leaf area yellow		1.00	-.19	-.04	-.36**	-.35**
Plant height			1.00	.16*	.31**	.14
Leaf width				1.00	.29**	.17*
Top weight					1.00	.86**
Root weight						1.00
Seed weight						
Seed count						
Cob weight						
Wt of 1st leaf sample						
P content of 1st leaf sample						
Wt of 2nd leaf sample						
P content of 2nd leaf sample						
% P in 3rd leaf sample						
Total plant weight						
100-seed weight						
Top-root ratio						
% P in 1st leaf sample						
% P in 2nd leaf sample						

[a]Coefficients are based on 158 to 160 degrees of freedom or 86 degrees of freedom with the coefficients that are underlined.

*,**Indicate significance at 5% and 1% levels, respectively.

Seed weight	Seed count	Cob weight	Wt of 1st leaf sample	P content, 1st leaf sample	Wt of 2nd leaf sample	P content, 2nd leaf sample	% P in 3rd leaf sample
-.50**	-.48**	-.36**	-.31**	-.04	-.03	.20**	.31**
-.46**	-.41**	-.30**	-.41**	-.06	.06	.19*	.35**
.33**	.24**	.23**	.13	.17*	.16*	.04	-.01
.23**	.24**	.35**	.27**	.39**	.31**	.17*	-.22*
.42**	.47**	.66**	.44**	.63**	.51**	.31**	-.01
.40**	.40**	.71**	.39**	.63**	.48**	.30**	-.02
1.00	.76**	.61**	.29**	.37**	.09	-.02	-.06
	1.00	.48**	.35**	.49**	.11	.06	-.11
		1.00	.34**	.63**	.50**	.36**	-.14
			1.00	.41**	.21**	.03	-.57**
				1.00	.59**	.59**	-.01
					1.00	.66**	.13
						1.00	.33**
							1.00

Table 47. (Continued)

weight	Total plant weight	100-seed weight	Top-root ratio	% P in 1st leaf sample	% P in 2nd leaf sample
% of leaf area dead	-.54**	.06	.28**	.21**	.24**
% of leaf area yellow	-.51**	.01	.31**	.24**	.21**
Plant height	.32**	.07	.03	.09	-.09
Leaf width	.24**	-.06	-.01	.23**	-.05
Top weight	.91**	-.14	-.64**	.32**	-.07
Root weight	.87**	-.05	-.88**	.36**	-.05
Seed weight	.74**	.17*	-.22**	.13	-.12
Seed count	.66**	-.51**	-.14	.20**	-.04
Cob weight	.83**	.10	-.59**	.42**	.02
Wt of 1st leaf sample	.45**	-.12	-.29**	-.26**	-.17*
P content of 1st leaf sample	.64**	-.24**	-.39**	.77**	.26**
Wt of 2nd leaf sample	.41**	-.03	-.38**	.48**	-.01
P content of 2nd leaf sample	.17*	-.13	-.13	.61**	.74**
% P in 3rd leaf sample	-.05	.07	.07	.50**	.34**
Total plant weight	1.00	-.01	-.65**	.25**	-.16*
100-seed weight		1.00	-.11	-.14	-.11
Top-root ratio			1.00	-.13	.18*
% P in 1st leaf sample				1.00	.40**
% P in 2nd leaf sample					1.00

C. Response of Corn and Soybeans to Foliar Applications of Phosphates by Brushing, Experiment 14

1. Introduction

The quantities of the phosphorus-nitrogen compounds available were not enough to do a complete plant-spraying experiment. There was enough material, however, to treat the plants by brushing on the solutions. It was thought that some evaluation of these compounds could be obtained by brushing the solutions on young plants twice and then measuring growth response by a dry-weight determination.

Neutral solutions of the ammonium salts of orthophosphoric acid and tripolyphosphoric acid were included among the treatments to make possible a comparison with these compounds that had been used in most other experiments.

2. Procedure

Hark soybeans were planted on March 29, 1973, in a low-phosphorus soil mixture in No. 10 cans. The soil was fertilized with 1.5 g of ammonium nitrate and 0.8 g of potassium nitrate per can. There were six replicates of the experiment with corn and seven of the experiment with soybeans. A completely randomized block design was used. Corn plants showed such severe symptoms of phosphorus deficiency on April 25 that the soil was treated with a solution to supply 6 ppm of phosphorus in the form on monobasic potassium phosphate.

On May 7, the plants were in healthy but slightly phosphorus-deficient state, and freshly prepared phosphorus solutions were applied to both sides of the leaves by means of a soft brush. The total amount of phosphorus applied per replicate of one corn plant was estimated at 8.6 mg (a total of 7 ml of a solution containing 0.74% phosphorus applied to six plants). The total amount of phosphorus applied per replicate of one soybean plant was estimated at 9.5 mg (a total of 18 ml of solution containing 0.37% phosphorus applied to seven plants). All solutions contained 0.1% Tween-80.

It was estimated that about 2/3 of the solution added was retained by the leaves and that the remainder dripped off. Thus the amounts of phosphorus retained on the plants may be estimated as about 5.7 mg per corn plant and 6.3 mg per soybean plant. To prevent the drops of solution falling from the leaves from reaching the soil, the pots were covered with paper at the time of application.

The applications were made in the greenhouse laboratory room under artificial light after the plants had been adjusted there for several hours.

All phosphorus compounds were applied at equal concentrations on a given crop. The maximum concentration was thus set by orthophosphate. Even the low concentration of 0.37% phosphorus caused a damage of 15 to 25% dead leaf tissue on soybeans on May 10, as estimated from the three most damaged leaves. The sensitivity of the soybean plants may have resulted from the method of application, which probably caused some broken leaf hairs. Perhaps another possibility is the fact that the soybeans were definitely deficient in phosphorus.

The phosphorus treatments were repeated on May 19. This time the corn received 13.6 mg of phosphorus per plant (11 ml of solution containing 0.74% phosphorus per six plants), and the soybeans received 6.1 mg of phosphorus per plant (17 ml of solution containing 0.25% phosphorus per seven plants). No leaf damage occurred following the second spray treatments.

The total dry plant weight was determined by cutting the plants at ground level on June 15 and drying them at 65°C.

3. Results and discussion

a. Corn Table 48 gives the yields of the plants, the weights of equal leaf areas from leaf discs obtained 11 days after the first application, the phosphorus content of the leaf samples, the phosphorus percentage in the leaf samples, and the total amount of phosphorus in the above-ground plant tissue. This last figure was calculated on the assumption that the phosphorus percentage in all the above-ground plant tissue was the same as that in the samples of the youngest mature unsprayed leaf.

Analyses of variance of the data are given in Table 49. The effects of the phosphorus treatments are significant with all measurements, and Duncan's multiple-range test was therefore applied to the means. The results of this test are presented in Table 48.

Table 48. Response of corn to phosphate solutions brushed on the leaves in Experiment 14[a]

Phosphorus solution brushed on the leaves	Plant weight (g)	Weight of leaf samples (mg)	P in leaf samples (μg)	% P in leaf samples	Total P in plants (mg)
Control	13.83 c	11.7 b	22.5 b	0.19 b	26.74 c
Ammonium orthophosphate	20.48 ab	12.9 ab	26.5 ab	0.21 ab	43.65 ab
Ammonium tripolyphosphate	19.82 ab	12.6 ab	26.4 ab	0.21 ab	41.51 abc
Phosphoryl triamide	22.73 a	13.5 a	31.0 a	0.23 a	52.85 a
Phosphonitrilic hexaamide	16.25 bc	12.8 ab	29.9 ab	0.21 ab	34.02 bc
Ammonium trimetaphosphimate	20.47 ab	13.1 a	31.4 a	0.24 a	48.39 ab

[a]Means in a given column not followed by one or more common letters differ significantly at the 5% level.

Table 49. Mean squares and levels of significance derived from analyses of variance of measurements of various characteristics of corn in Experiment 14 in which solutions of different phosphates were brushed on the leaves

		Mean squares and levels of significance				
Source of variation	d.f.	Plant Plant weight	Weight of leaf samples	P in leaf samples	% P in leaf samples	Total P in plants
Blocks	5	17.85	7.07×10^{-7}	29.79	0.0012	103.13
P treatments	5	65.93*	2.11×10^{-6}+	66.70*	0.0018*	545.21**
Error	25	21.94	9.60×10^{-7}	16.33	0.0069	146.33
C.V. (%)		24.63	7.69	14.71	12.26	29.37

+,*,**Indicate significance at 10%, 5%, and 1% levels, respectively.

Phosphoryl triamide gave the highest yield of above-ground plant material. According to the multiple-range test, the yield was significantly higher than the control and the phosphonitrilic hexaamide treatment, but it did not differ significantly from the yields obtained with ortho- and tripolyphosphate and ammonium trimetaphosphimate.

Phosphoryl triamide also had the highest sample weight, and it was significantly higher than that of the control treatment. In this experiment, all the samples were taken within an hour, and the variation among the replications of a given treatment was much smaller than the variation among the means of different treatments. Differences in sample weight are likely to be caused by differences in the soluble carbohydrate content, which would be expected to be positively correlated with the plant weight, the phosphorus content of the samples, and the calculated "total phosphorus content" of the plants (see Table 50).

Only phosphoryl triamide and trimetaphosphimate had a significantly higher phosphorus content in the leaf sample and a significantly higher phosphorus percentage in the sample than did the control treatment 10 days after the first application. Values for these two compounds, however, do not differ significantly from the corresponding values for the other phosphorus treatments, which agrees with an earlier observation that the translocation of various phosphorus compounds was relatively fast and equally good. In this experiment, the

Table 50. Correlation coefficients between the response of corn to phosphate solutions brushed on the leaves in Experiment 14[a]

	Plant weight	Weight of leaf samples	P in leaf samples	% P in leaf samples	Total P in plants
Plant weight	1.000	.522**	.403**	.240	.915**
Weight of leaf samples		1.000	.666**	.307+	.522**
P in leaf samples			1.000	.913**	.680**
% P in leaf samples				1.000	.591**
Total P in plants					1.000

[a]Correlations are based on 34 degrees of freedom.

+,**Indicate significance at 10% and 1% levels, respectively.

phosphorus percentage in the leaves of plants with all treatments was in the deficiency range suggested by deMooy et al. (1973). This finding agrees with the visual observation that the plants were deficient in phosphorus.

The difference between the calculated total amounts of phosphorus in the above-ground parts of the plants on the control and the phosphoryl triamide treatments is 26.1 mg, which is much more than the estimated quantity of 5.7 mg of phosphorus applied in the first treatment. This observation probably signifies only that in this experiment with young, phosphorus-deficient plants, there was a decided preferential translocation of phosphorus to the newly developing leaves.

b. <u>Soybeans</u> The results are presented in Tables 51 through 53. The soybeans were not phosphorus deficient, as may be inferred from the phosphorus percentage of leaf discs from the control treatment, but they did not grow well. The plants treated with orthophosphate suffered some damage from the orthophosphate solution applied to the leaves in the first treatment.

In this experiment, the only significant differences were among plant weights and calculated values of total phosphorus content obtained with the various phosphate treatments. Because of the difficulties mentioned in the preceding paragraph and the absence of positive or negative responses there is little justification for discussing in detail the differences among the various phosphorus treatments. The results of the experiment were included, however, for two reasons. First, the experiment showed that phosphoryl triamide and phosphonitrilic hexaamide caused no visual damage to the leaves, whereas a neutral solution of ammonium orthophosphate was definitely damaging when applied in a concentration to supply an equal concentration of phosphorus. Second, the maximum increase in the calculated amount of total phosphorus per plant from treatment with phosphorus solutions was only 5.2 mg, which is smaller than the estimated 6.2 mg of phosphorus retained by the plants in the first treatment. This

Table 51. Response of soybeans to phosphate solutions brushed on the leaves in Experiment 14[a]

Phosphate solution brushed on the leaves	Plant weight (g)	Wt of leaf samples (mg)	P in leaf samples (μg)	% P in leaf samples	Total P in plants (mg)
Control	10.53 ab	26.9	98.7	0.37	39.33 abc
Ammonium ortho-phosphate	9.58 b	28.4	91.6	0.32	31.20 c
Ammonium tripoly-phosphate	9.23 b	25.1	94.3	0.38	34.25 bc
Phosphoryl triamide	11.94 a	25.9	89.9	0.35	41.56 ab
Phosphonitrilic hexaamide	10.43 ab	26.7	96.7	0.36	37.78 abc
Ammonium trimeta-phosphimate	11.57 a	25.2	96.5	0.39	44.54 a

[a]Means in a given column not followed by one or more common letters differ significantly at the 5% level.

Table 52. Mean squares and levels of significance derived from analyses of variance of measurements of various characteristics of soybeans in Experiment 14 in which solutions of different phosphates were brushed on the leaves

Source of variation	d.f.	Mean squares and levels of significance				
		Plant weight	Weight of leaf samples	P in leaf samples	% P in leaf samples	Total P in plants
Blocks	6	1.13	1.03×10^{-5}	94.48	0.0018	18.43
P treatments	5	7.94*	7.87×10^{-6}	77.86	0.0039	164.49*
Error	30	2.50	7.76×10^{-6}	169.93	0.0022	53.69
C.V. (%)		14.98	10.65	13.78	13.07	19.23

*Indicates significance at 5% level.

Table 53. Correlation coefficients between the response of soybeans to phosphate solutions brushed on the leaves in Experiment 14[a]

	Plant weight	Weight of leaf samples	P in leaf samples	% P in leaf samples	Total P in plants
Plant weight	1.000	-.006	.032	.000	.794**
Wt of leaf samples		1.000	.431**	-.422**	-.246
P in leaf samples			1.000	.629**	.408**
% P in leaf samples				1.000	.599**
Total P in plants					1.000

[a]Correlations are based on 40 degrees of freedom.

**Indicates significance at 1% level.

observation indicates that the preferential movement of phosphorus from older parts to the newly developing leaves was less pronounced in the soybean plants, which had an adequate supply of phosphorus and which were developing pods, than in the young phosphorus-deficient corn plants in the preceding experiment.

VII. COMPLETE FOLIAR NUTRITION WITH PHOSPHORUS, EXPERIMENT 15

A. Introduction

The objective of this experiment was to determine whether corn and soybeans could be grown to maturity when the phosphorus they require is supplied by sprays and is not absorbed by the roots.

B. Procedure

Corn and soybeans were planted on June 5, 1972, in 10-gallon metal containers filled with pea-size gravel. The cans were coated with asphalt paint on the inside and had drainage holes in the bottom. The cans were watered daily, and, in warm weather, twice per day, with a complete Hoagland solution for the control treatment and a minus-phosphorus nutrient solution for the spray treatments. There were three spray treatments: (a) control (sprayed with 0.1% Tween-80), (b) sprayed with a 0.3% P solution of ammonium orthophosphate at pH 7.0, and (c) sprayed with a 0.3% P solution of ammonium tripolyphosphate at pH 7.0. The plants were located out of doors between the Agronomy greenhouses, and the experiment was arranged in a completely randomized block design with four blocks.

The first spray treatment was applied on June 24, and the spraying was repeated twice per week until August 27. The cans were carefully covered with plastic around the plant stems while they were sprayed. After each rain shower, when there was the possibility that some of previously foliar-applied phosphorus had dripped off the leaves into the root medium, the gravel was rinsed through with excess water.

The top leaf was covered with a plastic bag during the spray treatments after July 28 to prevent this leaf from receiving any phosphorus spray. Samples of these leaves were taken on August 12 by pinching three discs of 1.8 cm^2 with a cork borer. The leaf samples were taken within a half-hour period, dried, and weighed.

Watering of the plants was stopped on September 14, and the individual plants were harvested on September 20. Tops and roots were separated and dried to determine their dry weight.

C. Results and Discussion

An important error was made in this experiment. The plants on plus-phosphorus nutrient solution were supplied with phosphorus from the beginning, whereas the plants that received their phosphorus by spraying did not receive the first phosphorus spray until the plants were 19 days old. By this time, the plants showed symptoms of phosphorus deficiency and were behind in growth in comparison with the plants on the complete nutrient solution. It appeared to be difficult to get a significant amount of phosphorus into the very young plants by spraying, and the sprayed plants never caught up with the plants grown in a complete nutrient solution. Although this may have been an unfortunate error as far as the experiment is concerned, it may contain the lesson that, if foliar application of phosphorus ever becomes practical, plants grown on soil that is strongly deficient in phosphorus should receive a band or "starter" application of phosphorus to prevent deficiencies while the plants are small.

1. Corn

The mean values of all measured characteristics are given in Table 54, and the analyses of variance and possible statistical significance are given in Table 55. The treatment effect is highly significant for all variables, and the total sum of squares is divided into three orthogonal comparisons, most of which are also highly significant. Results of Duncan's multiple-range test are presented in Table 54.

The plants grown on the plus-phosphorus nutrient solution had the highest value for all variables except for the top-root ratio, as could be expected. Poor pollination of the plants receiving the phosphorus spray treatments, which tasseled later, especially those sprayed with tripolyphosphate, may have been another reason the yields were so much lower than those obtained with the complete nutrient solution. Plants receiving the orthophosphate treatment had higher values than the tripolyphosphate treatment for seed weight, number of

Table 54. Values of various characteristics of corn plants in Experiment 15 on complete foliar nutrition of plants with phosphorus, and results of Duncan multiple-range tests on the data[a]

Characteristics measured	Control (0.1% Tween-80)	P in nutrient solution	Ortho-phosphate spray	Tripoly-phosphate spray
Seed weight per plant (g)		160.8 a	99.6 b	42.9 c
Number of seeds per plant		562 a	437 b	247 c
100-seed weight (g)		27.7 a	22.9	17.4 c
Cob weight per plant (g)		30.9 a	21.9 b	17.9 b
Top weight per plant (g)	8.6 c	82.2 a	59.8 b	54.8 b
Root weight per plant (g)	2.4 c	31.6 a	17.6 b	21.3 b
Top-root ratio	4.5 d	9.7 b	11.4 a	6.6 c
Total weight per plant (g)	11.2 d	305.5 a	198.9 b	136.8 c
Plant height (cm)	82.0 b	184.5 a	184.5 a	180.3 a
Leaf width (cm)	3.4 c	7.1 a	6.1 b	5.4 b
Leaf sample weight (g)	.0174 d	.0311 a	.0289 b	.0256 c
P in leaf sample (μg)	15.1 d	98.1 a	64.7 b	27.7 c
P in leaf sample (%)	.087 c	.315 a	.225 b	.109 c

[a]Means of values in a given row not followed by one or more common letters differ significantly at the 5% level by the Duncan multiple-range test.

Table 55. F-values and level of significance of measurements of various characteristics of corn plants in Experiment 15 on complete foliar nutrition of plants with phosphorus

Source of variation[a]	d.f.	F-values and significance level of			
		Top weight	Root weight	Top-root ratio	Total plant weight
Blocks	3	<1	<1	21	1.25
Treatments	3	66.91**	74.61**	55.40**	211.37**
Comparison 1	(1)	29.04**	50.63**	1.99	176.55**
Comparison 2	(1)	<1	3.44+	69.01**	26.96**
Comparison 3	(1)	170.80**	169.77**	95.20**	430.60**
Error	9				
Coeff. of variation		14.71	15.39	11.64	10.38
		F-values and significance level of differences in measurements of characteristics with missing date for the control treatment			
		Seed weight	Seed count	100-seed weight	Cob weight
Blocks	3	4.37+	1.48	<1	<1
Treatments	2	254.32**	36.63**	55.15**	21.43**
Comparison 1	(1)	391.03**	46.96**	83.73**	38.90**
Comparison 1	(1)	117.64**	26.31**	26.55**	3.98+
Error	6				
Coeff. of variation		7.31	12.63	6.65	12.26

[a]Comparison 1 is spray treatments vs phosphorus in the nutrient solution; Comparison 2 is orthophosphate spray treatment vs tripolyphosphate spray treatment; Comparison 3 is control treatment vs the other three treatments.

+,*,**Indicate significance at 10%, 5%, 1%, respectively.

differences in measurements of characteristics with all data present

Plant length	Leaf width	Leaf sample weight	P content in leaf sample	% P in leaf sample
<1	21	21	1.10	<1
57.36**	40.06**	161.21**	127.54**	123.04**
<1	20.21**	43.84**	161.96**	159.74**
<1	3.39+	24.47**	61.70**	73.16**
171.83**	96.55**	415.31**	158.89**	135.98**
8.46	9.08	3.67	12.94	10.44

seeds, 100-seed weight, total plant weight, leaf sample weight, percent phosphorus in the leaves, and top-root ratio.

The phosphorus percentage in the leaves of the plants receiving the nutrient solution containing phosphorus was 0.315, which is sufficient. Leaf samples from plants receiving the orthophosphate spray treatment contained 0.225% P, which is low. But samples from plants receiving the tripolyphosphate spray treatment contained only 0.109% P, a value not significantly different from the phosphorus percentage in the leaves of plants that received no phosphorus in either the nutrient solution or in the spray. Although the plants sprayed with tripolyphosphate solution yielded 12 times as much as those without added phosphate, the phosphorus content of the unsprayed portion of the leaf area was near the minimum percentage.

With orthophosphate, the symptoms of phosphorus deficiency disappeared rapidly after the first spray treatments. Plants sprayed with tripolyphosphate, however, never lost their symptoms of phosphorus deficiency. These observations suggest that some of the phosphorus supplied as tripolyphosphate tended to persist in the plants as polyphosphate and hence was not available for metabolic use as was the phosphorus supplied as orthophosphate. The low phosphorus percentage in the unsprayed leaves of the tripolyphosphate-sprayed plants suggests further that the translocation of the polyphosphate through the considerable distance necessary to supply new leaves may also have been less than would be expected from the previous observations on the effectiveness with which phosphorus supplied as tripolyphosphate was translocated by corn plants from the small areas covered by the leaf discs.

The weights of equal areas of leaf samples are highly correlated with the yield and the phosphorus content of the leaves, as can be seen in Table 56.

The correlations between the weights of roots and tops were highly significant for the control without phosphorus ($r = 0.97$) and the tripolyphosphate treatment ($r = 0.88$) but were not significant for the two treatments which had a more ample supply of phosphorus.

2. Soybeans

The analytical and statistical data for all the measured characteristics are presented in Tables 57 through 59. The top weight does not include the leaves which had fallen at the time of harvest.

The treatment in which phosphorus was included in the nutrient solution had the highest values of all measured characteristics except the weight of the leaf sample. The 100-seed weight is the only characteristic with which the nutrient solution supplying phosphorus did not produce significantly greater numerical values than those obtained with the phosphorus spray treatments.

The highest yield of seed was obtained with orthophosphate

Table 56. Simple correlation coefficients among measurements of characteristics of corn plants in Experiment 15 on complete foliar nutrition of plants with phosphorus

	Plant height	Leaf width	Top weight	Root weight	Leaf sample weight	P content in leaf samples
Plant height	1.000	.894**	.895**	.828**	.892**	.649**
Leaf width		1.000	.956**	.882**	.943**	.869**
Top weight			1.000	.962**	.960**	.858**
Root weight				1.000	.895**	.804**
Leaf sample weight					1.000	.872**
P content in leaf sample						1.000
% P in leaf sample						
Seed weight						
Seed count						
Cob weight						
Total plant weight						
100-seed weight						
Top-root ratio						

[a]There are 14 degrees of freedom for the underlined values and 10 degrees of freedom for the others.

+,*,**Indicate significance at 10%, 5%, and 1% levels, respectively.

% P in leaf sample	Seed weight	Seed count	Cob weight	Total plant weight	100-seed weight	Top-root ratio
.622**	.411	.516+	.477	.814**	.203	.744**
.852**	.885**	.868**	.881**	.954**	.799**	.810**
.829**	.865**	.804**	.954**	.970**	.782**	.744**
.769**	.671*	.540+	.797**	.930**	.653*	.569*
.842**	.948**	.909**	.875**	.958**	.931**	.854**
.996**	.987**	.949**	.940**	.952**	.935**	.790**
1.000	.982**	.954**	.925**	.933**	.927**	.791**
	1.000	.968**	.925**	.984**	.940**	.607*
		1.000	.849**	.932**	.843**	.718**
			1.000	.968**	.879**	.395
				1.000	.922**	.790**
					1.000	.533+
						1.000

Table 57. Values of various characteristics of soybean plants in Experiment 15 on complete foliar nutrition of plants with phosphorus, and results of Duncan multiple-range tests on the data[a]

Characteristics measured	Control (0.1% Tween-80)	P in nutrient solution	Ortho-phosphate spray	Tripoly-phosphate spray
Seed weight per plant (g)	1.7 d	73.5 a	27.5 b	8.1 c
Number of seeds per plant	16 d	479 a	195 b	56 c
100-seed weight (g)	10.5 b	15.4 a	14.1 a	14.5 a
Top weight per plant (g)	4.8 c	56.6 a	23.2 b	9.7 c
Root weight per plant (g)	1.8 c	14.7 a	8.3 b	3.2 c
Top-root ratio	3.6 c	8.9 a	6.1 b	5.7 b
Total weight per plant (g)	8.3 c	144.8 a	59.0 b	21.0 c
Leaf sample weight (g)	.0321 ab	.0290 c	.0295 bc	.0325 a
P in leaf sample (μg)	23.4 b	116.1 a	33.1 b	35.5 b
P in leaf sample (%)	.073 b	.401 a	.112 b	.110 b

[a]Means of values in a given row not followed by one or more common letters differ significantly at the 5% level of the Duncan multiple-range test.

Table 58. F-values and level of significance of measurements of characteristics of soybean plants in Experiment 15 on complete foliar nutrition of plants with phosphorus

		F-values			
Source of variation[a]	d.f.	Seed weight	Seed count	100-seed weight	Top weight
Blocks	3	1.04	1.03	<1	<1
Treatments	3	363.41**	358.16**	6.92*	109.33**
Comparison 1	(1)	713.29**	679.58**	1.16	215.55**
Comparison 2	(1)	65.37**	78.47**	<1	18.18**
Comparison 3	(1)	311.55**	316.43**	19.53**	94.28**
Error	9				
Coeff. of variation		12.30	11.89	11.87	18.97

[a]Comparison 1 is spray treatments vs phosphorus in nutrient solution; Comparison 2 is orthophosphate spray treatment vs tripolyphosphate spray treatment; Comparison 3 is control treatment vs the other three treatments.

+,*,**Indicate significance at 10%, 5%, and 1% levels, respectively.

and significance level

Root weight	Top-root ratio	Total plant weight	Leaf sample weight	P content in leaf sample	% P in leaf sample
<1	1.67	<1	<1	<1	<1
89.86**	72.84**	210.84**	4.22**	99.69**	93.06**
139.90**	90.90**	406.90**	3.49++	240.10**	224.60**
34.89**	1.31	40.29**	6.01*	<1	<1
94.87**	126.36**	185.31**	3.18++	58.82**	54.46**
17.53	7.27	14.56	5.78	16.58	18.18

Table 59. Simple correlation coefficients among measurements of characteristics of all soybean plants in Experiment 15 on complete foliar nutrition of plants with phosphorus[a]

	Top weight	Root weight	Seed weight	Seed count	Total plant weight	100-seed weight	Top-root ratio	Leaf-sample weight	P content in leaf samples	% P in leaf samples
Top weight	1.000	.980**	.993**	.992**	.998**	.555*	.894**	-.650**	.901**	.908**
Root weight		1.000	.982**	.982**	.986**	.603*	.867**	-.698**	.847**	.858**
Seed weight			1.000	.998**	.999**	.574*	.905**	-.648**	.926**	.932**
Seed count				1.000	.998**	.556*	.910**	-.676**	.917	.928**
Total plant weight					1.000	.572*	.900**	-.655**	.911**	.919**
100-seed weight						1.000	.630**	-.212	.513*	.496*
Top-root ratio							1.000	-.535*	.878**	.875**
Leaf-sample weight								1.000	-.496*	-.553*
P content in leaf samples									1.000	.996**
% P in leaf samples										1.000

[a]There are 14 degrees of freedom for the measurements.

*,**Indicate significance at 5% and 1% levels, respectively.

supplied in the nutrient solution, second highest with the orthophosphate spray, and third highest with the tripolyphosphate spray. The relative differences among these seed yields are greater than those with corn in the same experiment. Plants receiving the orthophosphate treatment had a significantly higher seed weight, seed count, top weight, root weight, and total plant weight than did those receiving the tripolyphosphate treatment. With both soybeans and corn, therefore, the repeated sprays with orthophosphate performed better than those with tripolyphosphate in plant production. The content of phosphorus in the leaf samples from unsprayed leaves of the sprayed plants was very low and did not differ significantly from the corresponding values in the controls that were not supplied with phosphorus.

Table 59 gives the simple correlation coefficients. The weights of the leaf samples negatively correlated with all other characteristics. If an increase in sample weight is caused mainly by an increase in soluble carbohydrate, the implication is that the soluble carbohydrate content is inversely related to all the other characteristics, including the content of phosphorus in the leaves. Dunphy (1972) found an inverse relationship of water-soluble carbohydrate with phosphorus and potassium content of soybean plant tissue. Differences exceeding 1% in water-soluble carbohydrate content of leaves were noted in comparisons involving both phosphorus and potassium.

VIII. EVALUATION OF SEVERAL PHOSPHATES AS FOLIAR SPRAYS IN THE FIELD, EXPERIMENT 16

A. Introduction

Experimentation in the greenhouse involves growing plants under artificial conditions that differ from those in the field with respect to a number of environmental factors such as air humidity, dew formation, and temperature that may have an important effect on the performance of foliar applications of nutrients. Field tests are indispensable for practical evaluations. Because of large variations in conditions from region to region and from year to year, field experimentation also has its limitations, and extensive field experiments at different locations over several years are required for adequate evaluation. Because only limited quantities of the most promising condensed phosphates could readily be produced with the laboratory-scale equipment available only one small field experiment was feasible.

B. Materials and Methods

The experimental site was on the Bruner farm, 5 miles west of Ames, Iowa. The soil was a Webster silt loam. Tests of samples taken in mid-April, 1972, showed a pH of 6.7, 17 to 28 pp2m of phosphorus extractable by the Bray No. 1 method, and 142 pp2m of exchangeable potassium. The value for phosphorus is classed as low.

Two strips of corn, 15 rows in width by 100 meters in length were planted on May 10, 1972. Individual rows were spaced 75 cm apart. The variety was Pioneer 3369A, a long-season variety with high yield potential. The soybeans, variety Wayne, were planted on May 11 in 30-cm rows in a strip of 72 rows between the two strips of corn. The corn received 255 kg of nitrogen per hectare before planting, and the soybeans received no fertilizer.

The spray treatments were control and ortho-, tripoly-tetrapoly-, trimeta-, and tetrametaphosphate. All solutions contained 0.1% Tween-80 and were neutralized to pH 7.0 with ammonium hydroxide before application. The treatments were applied by means of a hand-pump sprayer. The leaves were sprayed from below and above in such a way as to cause adherence of a maximum amount of solution with relatively little loss by dripping. The spraying was done after sunset between 8 and 10 p.m.

The experiment was arranged in a completely randomized block design with six blocks. The control treatment was replicated twice in each block. The corn plots were single rows 10 feet long and were thinned to 14 plants per plot. With soybeans, plots 7 feet long and 2 rows wide were used. All individual plots were surrounded by border rows.

All the condensed ammonium phosphates were freshly prepared in the laboratory according to procedures given in section IV. The first application was made on June 20, when the corn plants were about 2 feet tall, at 900 liters per hectare. The time of application was later than initially planned because of unstable weather conditions in the preceding week.

Leaf samples were taken from the unsprayed, full-grown young leaves on July 20. With corn, a leaf tip 30 cm long was taken from each plant in the plot. With soybeans, 15 leaflets were collected per plot.

Originally a second spraying was planned for both crops at the time of corn tasseling. The weather conditions were constantly so unstable, however, that it was decided to divide the available material and to apply it in two separate sprays of about half of the originally planned concentration to avoid the possibility of losing the second spray due to a rain shower. The second spray was applied on July 12 in 1700 liters per hectare. Because of frequent showers, the third spray was delayed until July 31 at 2300 liters per hectare.

During the last two spray treatments, the corn ears were covered with a plastic bag to protect the silk and husk leaves from the spray. On August 16, the top third of the second husk leaf was sampled for phosphorus analysis. Soybeans were sampled as before.

To ensure that the corn would have an adequate supply of nitrogen and potassium with the very wet spring and summer weather of 1972, it was decided on July 22 to side-dress the corn with extra nitrogen and potassium in amounts equivalent to 112 kg of each element per hectare. The fertilizer was ammonium nitrate and potassium nitrate dissolved in 2 liters of water per plot and applied in a furrow along one side of the row.

Soybeans were harvested on September 29, and the corn was picked on September 30.

C. Results and Discussion

1. Corn

The yield and phosphorus analysis data for corn are given in Table 60. Table 61 gives the F-values of the analyses of variance, and Table 62 gives the simple coefficients of variation.

Because of a wind and hail storm on July 14, some plants were broken and produced no ear or only a partly developed ear. The yield data are consequently reported in three ways: (a) the uncorrected yields, which show no significant difference at the 5% level according to Duncan's multiple-range test, (b) the yields corrected for the number of missing ears, and (c) the yields corrected for the number of missing ears and the number of abnormal ears. In (b), the yield with ammonium tripolyphosphate exceeds the yield of the control at the 5% level of significance. In (c), the yields obtained with both ammonium tripolyphosphate and ammonium tetrapolyphosphate exceed the yield of the control at the 5% level. There are no significant differences in the phosphorus percentages in the

Table 60. Spray concentrations, yields of grain, phosphorus percentages in unsprayed leaves, and number of ears per plot in Experiment 16 on corn grown in the field with foliar applications of phosphorus[a]

Phosphorus compound	Phosphorus concentration in spray solutions, %			Yield
	1st spray	2nd spray	3rd spray	Uncorrected
Control	0	0	0	9291 a (147.9)[c]
Ammonium orthophosphate	.96[d]	.36	.41	9983 a (158.9)
Ammonium tripolyphosphate	.95	.58	.49	10391 a (165.4)
Ammonium tetrapolyphosphate	.98	.57	.62	9298 a (148.0)
Ammonium trimetaphosphate	.83	.82	.80	9618 a (153.1)
Ammonium tetrametaphosphate	.94	.63	.58	9486 a (151.0)

[a]Means in a given column not followed by one or more common letters are statistically different at the 5% level.

[b]Based on 15.5% moisture.

[c]Numbers in parentheses give the yields of grain in bushels per acre.

[d]Ammonium orthophosphate was accidentally applied at twice the intended concentration.

of grain[b] (kg/ha)					
Corrected for miss-ine ears	Corrected for missing and abnor-mal ears	% P in leaves		Number of ears per plot	
		1st sampling	2nd sampling	Total	Normal
9983 b (158.9)	10234 b (162.9)	.333 a	.162 a	13.0	12.3
10341 ab (164.6)	10686 ab (170.1)	.342 a	.168 a	13.5	12.3
10793 a (171.8)	10994 a (175.0)	.349 a	.171 a	13.5	12.8
10692 ab (170.2)	10988 a (174.9)	.328 a	.165 a	12.2	11.3
10165 ab (161.8)	10667 ab 169.8)	.338 a	.159 a	13.2	11.8
10215 ab (162.6)	10523 ab (167.5)	.332 a	.172 a	13.0	12.0

Table 61. F-values and levels of significance derived from analyses of variance of yields of grain and phosphorus percentages in leaves of plants in Experiment 16 on corn grown in the field with foliar applications of phosphorus

		F-values and levels of significance				
		Yield of grain			% P in leaves	
Source of variation[a]	d.f.	Total	Corrected for missing ears	Corrected for missing and abnormal ears	1st sampling	2nd sampling
Blocks	5	3.15*	4.47**	6.33**	2.52*	3.35*
P treatments	5	1.08	1.68+++	2.22++	<1	<1
Comparison 1	(1)	1.55	4.05*	7.76**	<1	<1
Comparison 2	(1)	<1	4.11*	2.96+	<1	<1
Comparison 3	(1)	3.05+	<1	<1	1.48	<1
Comparison 4	(1)	<1	<1	<1	<1	<1
Comparison 5	(1)	<1	<1	<1	<1	<1
Error	31					
Coeff. of variation		11.25	6.44	5.30	8.89	13.66

[a]Comparison 1 is control vs phosphate spray treatments; Comparison 2 is tri- and tetrapolyphosphate vs tri- and tetrametaphosphate; Comparison 3 is tripolyphosphate vs tetrapolyphosphate; Comparison 4 is trimetaphosphate vs tetrametaphosphate; Comparison 5 is orthophosphate vs four other phosphate spray treatments.

+,*,**Indicate significance at 10%, 5%, and 1% levels, respectively.

++Indicates significance at 7.7% level.

+++Indicates significance at 16.7% level.

Table 62. Coefficients of simple correlation among yields of grain, phosphorus percentages in leaf samples, and numbers of ears per plot in Experiment 16 on corn grown in the field with foliar applications of phosphorus[a]

	Yield of grain			% P in leaves		Number of ears per plant	
	Uncorrected	Corrected for missing ears	Corrected for missing and abnormal leaves	1st sampling	2nd sampling	Total	Normal
Yield of grain							
Uncorrected	1.000	.742**	.702**	.312*	.335*	.795**	.777**
Corrected for missing ears		1.000	.898**	.373*	.367*	.186	.488**
Corrected for missing and abnormal years			1.000	.362*	.320*	.219	.233
% P in leaves							
1st sampling				1.000	.695**	.115	.288+
2nd sampling					1.000	.181	.356*
Number pf ears per plot							
Total						1.000	.700**
Normal							1.000

[a]There are 40 degrees of freedom in the various correlations.

+,*,**Indicate significance at 10%, 5%, and 1% levels, respectively.

leaves. All values, including the control, however, were relatively high. Evidently there was little phosphorus deficiency.

The correlation between the phosphorus percentages in the leaves and the yields is significant at the 5% level, but the correlation is not very high, as might be expected with the relatively high phosphorus percentages that were found.

2. Soybeans

The primary data obtained with soybeans are given in Table 63, and the statistical analyses are given in Tables 64 and 65.

The yields obtained do not differ significantly among treatments at the 5% level. Ammonium orthophosphate produced the lowest yield, even lower than the control, which may be a consequence of the leaf damage after the first spray. From 10 to 20% of the area of the three most severely damaged leaves was dead (with corn this was only 5%).

The phosphorus percentages in the leaves differ significantly at both samplings. In the first sampling, the highest value was obtained with ammonium orthophosphate, confirmed earlier findings that this compound was absorbed and translocated rapidly by soybeans. The phosphorus percentage in leaves treated with trimetaphosphate is also significantly lower than the phosphorus percentage in leaves treated with tetrametaphosphate. Plants receiving phosphorus sprays had higher phosphorus percentages in their top leaves than did plants on the control treatment at the second sampling.

Table 63. Spray concentrations, yields of grain, and percentages in unsprayed leaves of plants in Experiment 16 on soybeans grown in the field with foliar applications of phosphorus[a]

Phosphorus compound	Phosphorus concentration in spray solution, %			Yield of grain[b]		% P in leaves	
	1st spray	2nd spray	3rd spray	kg/ha	bu/acre	1st sampling	2nd sampling
Control	0	0	0	3749 a	55.7	.397 bc	.372 b
Ammonium orthophosphate	.96[c]	.36	.41	3608 a	53.6	.413 a	.411 a
Ammonium tripolyphosphate	.95	.58	.49	4005 a	59.5	.405 ac	.397 a
Ammonium tetrapolyphosphate	.98	.57	.62	3965 a	58.9	.393 bc	.395 a
Ammonium trimetaphosphate	.83	.82	.80	3682 a	54.7	.385 b	.412 a
Ammonium tetrametaphosphate	.94	.63	.58	3931 a	58.4	.405 ac	.408 a

[a]Means in a given column not followed by one or more common letters are statistically different at the 5% level.

[b]Based on 13% moisture.

[c]Ammonium orthophosphate was accidentally applied twice the intended concentration, which produced some leaf damage. No damage to the leaves was observed with the other phosphates.

Table 64. F-values of analyses of variance of yields of grain and phosphorus percentages in leaves of plants in Experiment 16 on soybeans grown in the field with foliar applications of phosphorus

		F- values and levels of significance		
			% P in leaves	
Source of variation[a]	d.f.	Yield of grain	1st sampling	2nd sampling
Blocks	5	1.05	5.69**	1.28
P treatments	5	<1	2.91*	5.29**
Comparison 1	(1)	<1	<1	22.68**
Comparison 2	(1)	<1	<1	2.78+
Comparison 3	(1)	<1	2.13	<1
Comparison 4	(1)	<1	5.57*	<1
Comparison 5	(1)	1.88++	5.93*	<1
Error	31			
Coeff. of variation		12.21	3.62	5.05

[a]See footnote to Table 61.

++,+,*,**Indicate significance at 18%, 10%, 5%, and 1% levels, respectively.

Table 65. Coefficients of simple correlation among yields of grain and phosphorus percentages in Experiment 16 on soybeans grown in the field with foliar applications of phosphorus

	Yield of grain	% P in leaves	
		1st sampling	2nd sampling
Yield of grain	1.000	.010	-.067
% P in 1st leaf sampling		1.000	.256+
% P in 2nd leaf sampling			1.000

+Indicates significance at 10% level.

IX. SUMMARY AND CONCLUSIONS

The objectives of the work described in this dissertation were: (a) to find phosphorus compounds which can be applied to the leaves without significant damage at a high enough concentration to contribute significantly to the phosphorus requirement of plants and which, at the same time, are absorbed well and available for plant metabolism; (b) to develop an experimental technique which would permit screening a large number of compounds quantitatively and qualitatively with respect to their suitability as a phosphorus source by means of spray application; (c) to determine if any yield responses could be obtained by using these compounds in treatments in field experiments; and (d) to evaluate some factors which are thought to have an important effect on foliar absorption.

Unpublished research performed in 1966 and 1969 by Dr. P. K. Hanley and by John Phillip, both former graduate students of Dr. C. A. Black, was reviewed. The author worked on this project from 1969 to 1974.

An experimental technique to screen a large number of phosphorus compounds was developed over the years 1966 to 1970 by Dr. Black's students. The method consisted of applying 25-microliter volumes of solution to leaf areas of 1.13 cm^2 delineated with a ring of paraffin and lanolin on the youngest most mature leaves of corn and soybean plants. The treated areas were rated visually to determine the degree and extent of the damage done to the leaves. Eventually, a cork borer a little larger than the ring was used to cut out the treated area for analysis. The phosphorus removed from the cut leaf disc by washing it with water was determined as a measure of the unabsorbed phosphate. The washed disc was then ashed to determine the total residual phosphorus content. By use of appropriate controls, it was possible to determine how much of the added phosphorus had been absorbed and how much of the absorbed phosphorus had been translocated out of the leaf disc.

It was learned from a review of the literature that orthophosphoric acid is one of the best compounds for foliar application. The quantity of phosphorus that can be applied to a crop in the juvenile stage with phosphoric acid, however, is only 1 to 2 kg per ha. After the observation was made that far greater amounts of urea (a nonionic compound) could be safely applied, Dr. P. K. Hanley decided to investigate the hypothesis that nonionic phosphorus compounds might be less toxic than ionic compounds. Various organic phosphates and potassium phosphate were applied to soybean leaves, and their absorption and damage to the leaves was measured 7 days after application. The results indicated that dimethyl, trimethyl, diethyl, triethyl, tripropyl, dibutyl, and tributyl phosphates are no better than monobasic potassium phosphate.

Hanley also investigated the effect of adding urea and/or sucrose to the solution of the phosphorus compound. Inclusion of sucrose in the solution applied to soybean leaves much reduced the severity of the damage to the leaves and the leaf area damaged from application of urea, and to a lesser extent, phosphorus. No damage was noted from sucrose alone. Sucrose had no apparent effect on the phosphorus absorption. Damage to the leaves from application of both orthophosphoric acid and urea exceeded the sum of the damage caused by the treatments individually. Urea did not seem to influence phosphorus absorption, but this was hard to judge with nearly all values for phosphorus absorption exceeding 90%.

After this experiment, it was concluded that the acidity of the phosphoric acid might be more responsible for the leaf damage than the concentration, and John Phillip investigated the influence of neutralization of phosphoric acid and addition of glycols to the applied phosphorus solutions. The phosphoric acid was applied in water or in water containing glycerol, ethylene glycol, diethylene glycol, or triethylene glycol; and it was unneutralized or neutralized to pH 7.0 with ethylamine, diethylamine, triethylamine, ethanolamine, triethanolamine or ammonium hydroxide. Only the neutralization of phosphoric acid with ammonium hydroxide produced a significant decrease in damage to the soybean leaves. None of the glucols proved to be beneficial with soybeans, but the combination of phosphoric acid and ethylene glycol produced less damage to corn leaves than did phosphoric acid alone. Ammonium hydroxide as a neutralizing agent produced the least damage on corn. There was less absorption of phosphorus from ammonium phosphate than from any other treatment, but the uptake of 78% of the applied phosphorus within 3 days after application was still good.

Some 35 different compounds were evaluated in seven screening experiments. Compounds were selected for testing on the basis of their ionic character, the rate at which they release phosphate, their ability to neutralize orthophosphoric acid and their associated properties. Certain organic bases and compounds which had not been tested before were tested in these experiments.

An important way of reducing the toxicity of phosphoric acid might be by lowering the solute suction per unit of phosphorus in the applied solution. Condensed phosphates as a group have this property. These substances are chain or ring compounds in which phosphate groups are joined with elimination of one molecule of water for each phosphate group added. The simplest ones are chain compounds like pyrophosphoric acid, tripolyphosphoric acid and tetrapolyphosphoric acid, having two, three, and four phosphate groups, respectively. Trimetaphosphoric acid and tetrametaphosphoric acid have, respectively, three and four phosphate groups in a ring structure. Others that contain mixtures of higher molecular weight phosphates, up to 10^4 to 10^6, are potassium metaphosphate and calcium metaphosphate.

Another group of phosphorus compounds that was considered very promising contains phosphorus-nitrogen bonds and phosphorus-nitrogen-phosphorus linkages. The nitrogen is present in the amide or imide form rather than as ammonium. These covalent compounds have a much lower ionic strength than orthophosphoric acid. One of these compounds, phosphoryl triamide, $PO(NH_2)_3$, is the phosphorus analog of urea. It is not appreciably ionized in water, but it is hygroscopic and gradually hydrolyzes with release of orthophosphate.

Both groups of compounds hydrolyze spontaneously to release orthophosphate, and all share the quality of delayed action.

Nearly all phosphorus compounds were applied in the ammonium form to avoid possible effects that different cations might have on phosphorus absorption. The plants were provided with an adequate nitrogen supply in the soil so that the effect of differing amounts of nitrogen supplied by various compounds could be neglected.

The condensed phosphates and phosphorus-nitrogen compounds proved to be the most promising compounds for foliar application. Tripolyphosphate was the best condensed phosphate on corn; 67% of the applied phosphorus was absorbed within 10 days; and 87% of the absorbed phosphorus was translocated outside of the treated area within the same period. Tetrapolyphosphate followed closely as the second best compound. These phosphorus sources could be applied at 2.5 to 3 times the quantity of phosphorus that could be applied as orthophosphate. Soybeans proved to be more sensitive than corn and could in general tolerate only 2/3 to 3/4 of the quantities of the various compounds that could be applied to corn, except for phosphonitrilic hexaamide, which could be applied at a higher concentration to soybeans than to corn and was absorbed well.

The ring compounds, tri- and tetrametaphosphate, could be applied in even greater quantities to corn (3 to 4 times that of orthophosphate) without causing damage, but their rate of absorption was much less than that of the polyphosphates, which makes them less desirable compounds than the polyphosphates.

Neutral solutions of ammonium tripolyphosphate and tetrapolyphosphate required up to several days to dry and crystallize after application of the solution to leaves of plants in the greenhouse. Initially these compounds were absorbed much less rapidly than the corresponding orthophosphate. The prolonged contact between the leaf and the syrup, however, probably permitted absorption to continue at an effective rate for a longer time than would have been the case had the solutions dried quickly. This behavior may be an important factor in the effectiveness of tri- and tetrapolyphosphate.

The delayed action is visually evident with phosphoryl triamide also. Initially, the compound is not readily absorbed. It crystallizes on the surface of the leaves. In the dry form, it does not damage the leaves. In 3 to 10 days, in the trials conducted in the greenhouse, the compound undergoes chemical alteration as a result of interaction with water, and the residue becomes a liquid. During this time, orthophosphate is being released and absorbed. Eventually, the liquid disappears. In the experiments reported, 41% of the added phosphorus was absorbed by corn in 10 days. Soybeans absorbed 65% over a 10-day period. Phosphonitrilic hexaamide has a ring structure and is a more complex compound than phosphoryl triamide. This compound acts like phosphoryl triamide in that it first crystallizes on the surface of the leaf, then liquifies and gradually disappears. The rate of liquefaction, however, is slower than that of phosphoryl triamide. Because this compound could be applied in a relatively large quantity without causing damage, especially to soybeans, it merits further investigation.

Other condensed phosphates, including some long-chain polyphosphates and ultraphosphates, were either absorbed to a low degree or translocated poorly.

Urea is a weak base and forms urea phosphate compounds with phosphoric acids. Three different urea phosphates were tried and were absorbed well, but caused more damage than regular condensed phosphates at high phosphorus concentrations.

Neutralization of orthophosphate with organic bases including choline, guanidine, and guanylurea did not prove useful as a technique for increasing the quantity of orthophosphate that could be applied without damage to the leaves.

Several organic phosphates were tested. These included creatine phosphate, creatinine phosphate, glucose-6-phosphate, fructose-1,6-diphosphate, adenosine phosphate, acetyl phosphate, carbamyl phosphate, ammonium phytate, and glycine ethyl ester phosphate. None of them were superior to the condensed phosphates.

The rapid intake of orthophosphate was suspected to be an important reason for the damage to the leaves that was observed with applications of no more than 120 to 150 μg of phosphorus per cm^2 to corn leaves and 60 to 90 μg of phosphorus per cm^2 to soybean leaves. Corn showed a high translocation (76% of the absorbed P) during the first 24 hours. Soybeans translocated less than 5% of the absorbed phosphorus during the first 24 hours. The rapid increase in concentration of phosphate in the cell solution might alter the cell pH or produce toxic effects in other ways.

To investigate the pH effect, orthophosphate and tripolyphosphate were applied at pH values ranging from 2 to 10. With both compounds and both crops there was more damage to the leaves at pH 2 than at pH 10, and there was significantly more damage at pH 10 than at pH 7. Within the range tested, the pH did not affect absorption and translocation of the phosphorus of orthophosphate by either corn or soybeans. Absorption of the phosphorus of tripolyphosphate by corn decreased with an increase in pH at both sampling times, but the percentage translocation of the phosphorus absorbed was not significantly influenced by the pH. This observation confirmed the finding in the phosphorus screening experiments that the translocation of absorbed phosphorus by corn was unaffected by the quantities of phosphorus applied and absorbed.

With soybeans, the absorption of phosphorus applied as tripolyphosphate decreased with an increase in pH of the phosphate solutions at both sampling times. The percentage translocation of the absorbed phosphorus decreased with an increase in the pH of the solutions in the sampling made after 10 days, but there was no evident effect after 24 hours, perhaps because of the relatively high experimental errors associated with measurements of the small amounts of phosphorus absorbed and translocated in the short time interval.

In an investigation of the experimental technique used to quantify the absorption and translocation, it was proven that spreading the phosphorus solution over the leaf surface with the fire-polished tip of a glass rod produced some increase in damage to the leaves of soybeans. The spreading action seemingly broke some of the leaf hairs. Corn plants have fewer and different hairs than do soybeans, and no increase in damage to the leaves of corn due to spreading of the phosphorus solutions was observed.

In an investigation of the response of genotypes, it was found that different genotypes of the same corn inbred line had a significant difference in tripolyphosphate absorption which is believed related to membrane permeability. No difference between genotypes was observed in orthophosphate absorption or in the translocation of phosphorus applied to the leaves as either orthophosphate or tripolyphosphate.

The maximum concentration of phosphorus of condensed phosphates that could be applied to plants in the greenhouse by spraying was determined, and the responses of plants to spraying with these phosphorus compounds were investigated. With soybeans the yields of plants sprayed with various phosphorus compounds significantly exceeded the yields of the unsprayed control with all phosphorus sources except tripolyphosphate. With tripolyphosphate there was considerable leaf damage, which was reflected in the relatively low weight per seed. The phosphorus was absorbed and translocated, however, as indicated by the high phosphorus percentage in the young, unsprayed leaves.

The quantities of the phosphorus-nitrogen compounds available were not enough to do a complete plant-spraying experiment, but there was enough material to treat the plants by brushing on the solution in one experiment. Phosphoryl triamide gave the highest yield of above-ground plant material with corn, but it was not significantly different from the yields obtained with ortho- and tripolyphosphate.

In another experiment it was proven that corn and soybean plants can be grown to maturity when all the phosphorus they require is supplied by sprays and is not absorbed by the roots. It was also learned that it may be difficult to prevent deficiencies while the plants are small.

Several different condensed phosphates were sprayed on corn and soybeans in a field experiment. An increase in yield of corn that was statistically significant at the 5% level was obtained from spraying. The yields with tripoly- and tetrapolyphosphate were, respectively, 760 and 754 kg/ha above the control yield of 10,234 kg/ha. There were no significant differences in the phosphorus percentages in the leaves, but all values including the control were relatively high. Evidently there was little phosphorus deficiency.

With soybeans, the increase in yield due to treatment was significant at the 18% level, and the increase was equivalent to 256 kg/ha above the control yield of 3747 kg/ha. The phosphorus percentages in the leaves were increased by the spray treatments. All leaves had a relatively high phosphorus percentage, which indicates that there was little deficiency of phosphorus in the plants.

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XII. APPENDIX

Table 66. Yields of grain, number of seeds per plant and 100-seed weights of soybeans receiving two and three sprays with various sources of phosphorus in Experiment 13[a]

Treatment[b]	Yield (g/plant)		Number of seeds per plant		100-seed weight	
	2 sprays	3 sprays	2 sprays	3 sprays	2 sprays	3 sprays
Control	21.7 ef	20.4 f	177 fg	164 fg	12.26 ab	12.51 ab
Orthophosphate spray	25.8 bc	25.0 bcd	205 bc	197 bcd	12.57 ab	12.71 a
Pyrophosphate spray	21.7 ef	24.1 cd	180 ef	206 bc	12.10 ab	11.71 ab
Tripolyphosphate spray	22.8 ed	20.1 f	192 cdef	184 edf	11.85 ab	10.95 b
Tetrapolyphosphate spray	25.5 bc	26.6 abc	200 bc	211 ab	12.74 a	12.64 ab
Trimetaphosphate spray	24.3 cd	24.2 cd	190 cdef	199 bcd	12.86 a	12.21 ab
Tetrametaphosphate spray	24.9 bcd	25.2 bcd	204 bc	194 bcde	12.21 ab	12.96 a
Polyphosphate mixture spray	25.9 bc	26.6 abc	206 bc	203 bc	12.58 ab	13.11 a
Na-Churs spray	25.7 bc	27.3 ab	207 bc	207 bc	12.44 ab	13.25 a
Orthophosphate in soil	28.0 a		221 a		12.71 a	

[a]Means in a given column not followed by one or more common letters differ significantly at the 5% level.

[b]All the sprays except Na-Churs were applied as neutral solutions of the ammonium salts.

332

Table 67. Characteristics of corn receiving two and three sprays with various sources of phosphorus in Experiment 13[a]

Treatment[c]	No. of sprays	Yield (g/ plant)	No. of seeds/ plant	100-seed weight (g)	Plant height (cm)
Control	2	109.2	394	27.9	262
	3	107.4	377	28.8	265
Orthophosphate spray	2	105.3	340	30.9	256
	3	106.5	359	29.7	256
Pyrophosphate spray	2	109.5	359	30.6	262
	3	105.2	369	28.6	258
Tripolyphosphate spray	2	107.9	373	29.2	251
	3	104.3	349	30.0	255
Tetrapolyphosphate spray	2	105.6	344	30.7	250
	3	105.9	352	30.2	258
Trimetaphosphate spray	2	93.0	317	29.4	255
	3	94.9	325	29.2	258
Tetrametaphosphate spray	2	106.3	376	28.4	253
	3	100.3	346	29.0	263
Polyphosphate mixture spray	2	92.4	313	29.5	242
	3	98.7	348	28.4	252
Na-Churs spray	2	107.7	348	28.8	260
	3	112.6	392	28.9	267
Orthophosphate in soil	0	118.1	433	27.3	265

[a]Means in a given column not followed by one or more common letters differ significantly at the 5% level.

[b]Leaf under ear.

[c]All the sprays except Na-Churs were applied as neutral solutions of the ammonium salts.

Leaf width[b] (cm)	Top weight (g)	Root weight (g)	Cob weight (g)	Total plant weight (g)	Top-root ratio	% P in leaf sample
8.7	80.3	16.0	18.5	224.0	14.1	.100
8.5	86.1	17.0	20.9	231.9	13.9	.078
8.0	78.0	16.1	17.9	217.3	13.8	
8.2	79.2	15.1	18.2	218.9	15.4	.266
8.1	78.9	16.9	19.2	224.5	13.5	
8.5	91.1	18.0	19.9	234.1	13.3	.236
8.3	81.5	20.9	18.2	228.4	11.4	
8.2	86.5	17.7	19.0	227.3	14.1	.201
8.3	75.8	17.0	18.2	216.5	13.2	
8.1	80.7	16.4	18.4	221.3	13.9	.254
8.0	70.4	14.6	14.7	192.7	13.6	
8.3	74.0	12.8	14.9	196.6	15.5	.273
8.2	73.2	14.4	17.8	211.7	15.4	
8.1	84.9	17.9	18.8	221.9	13.4	.271
8.0	70.7	14.0	16.0	193.1	15.1	
8.1	74.6	12.7	16.2	202.2	16.5	-
8.4	78.5	15.8	18.3	220.3	14.4	
8.4	84.8	16.5	19.9	233.8	15.0	.251
8.4	114.0	30.1	24.5	286.7	9.8	.259